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Evaluation of HCl Continuous Emission Monitors

Entropy Environmentalists, Inc.
Research Triangle Park, NC

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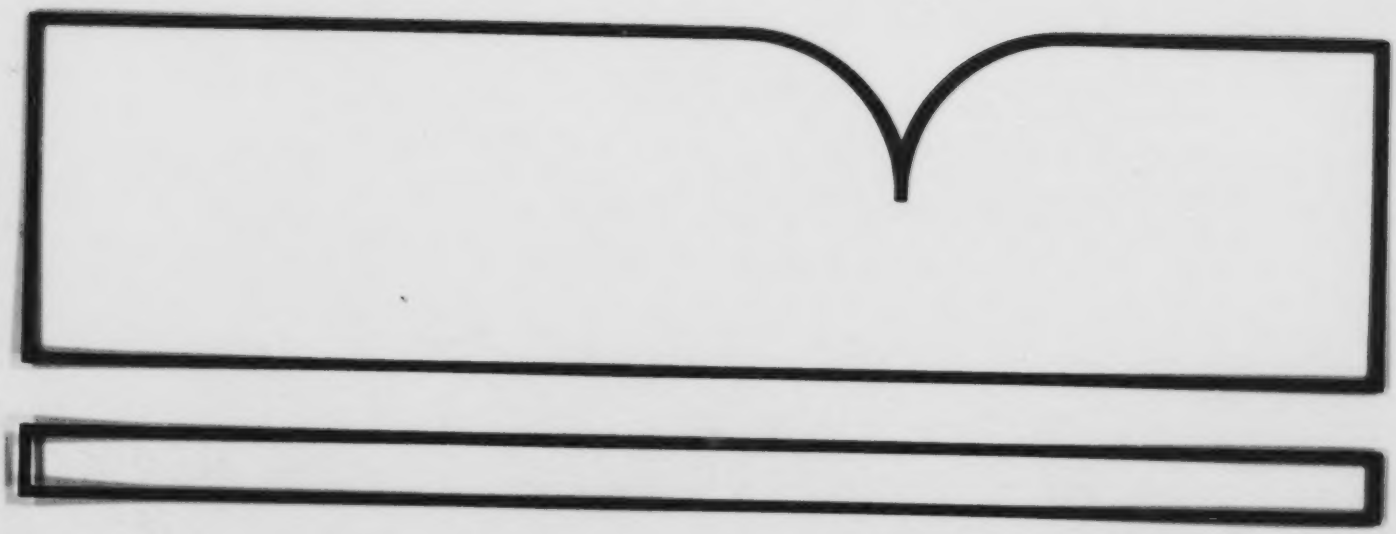

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EVALUATION OF HCl CONTINUOUS EMISSION MONITORS

by

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16. ABSTRACT

This report presents the findings obtained from the field evaluation of commercially available HCl monitoring equipment at a municipal waste-fired boiler which was not equipped with HCl emission control equipment. The analyzers were operated continuously during a two-month test period.

The measurement techniques employed by the HCl monitors evaluated were IR gas filter correlation, specific ion electrode, wet chemical colorimetric, dry reaction colorimetric, and gas membrane galvanic cell.

Except for the gas membrane galvanic cell monitor, the HCl monitoring equipment produced effluent measurements that were in good agreement with concurrent reference measurements. The results comparing the CEM data to the reference wet-chemistry measurement data do not indicate biases for any of the monitor measurement techniques because of analytical interferences present in the effluent of this municipal refuse-fired boiler. Also, both in-stack dilution systems and the nondilution, heat-traced sampling system were found to reliably provide representative effluent samples to the analyzers.

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ABSTRACT

Regulations currently exist limiting hydrogen chloride (HCl) emissions from various municipal and hazardous waste combustion sources. In addition, some states require that new or proposed incinerator facilities monitor HCl on a continuous basis to demonstrate continuous compliance with these HCl emission requirements. To determine whether this equipment can be used to accurately and reliably monitor uncontrolled and controlled HCl emissions on a continuous basis, the EPA contracted Entropy to conduct an evaluation of commercially available HCl monitoring equipment. This report presents the findings obtained from the field evaluation conducted at a municipal waste-fired boiler which was not equipped with HCl emission control equipment. The analyzers were operated continuously during a two month test period.

The measurement techniques employed by the HCl monitors evaluated were IR gas filter correlation, specific ion electrode, wet chemical colorimetric, dry reaction colorimetric, and gas membrane galvanic cell.

Except for the gas membrane galvanic cell monitor, the HCl monitoring equipment produced effluent measurements that were in good agreement with concurrent reference measurements. The results comparing the CEM data to the reference wet-chemistry measurement data do not indicate biases for any of the monitor measurement techniques because of analytical interferences present in the effluent of this municipal refuse-fired boiler. Also, both in-stack dilution systems and the nondilution, heat-traced sampling system were found to reliably provide representative effluent samples to the analyzers.

The project will be continued at a combustion source that includes HCl emission control equipment.

This report was submitted in fulfillment of Contract 68-02-4442 by Entropy Environmentalists, Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from May 1986 to May 1987 and work was completed as of August 1987.

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SECTION 1

INTRODUCTION

U.S. Environmental Protection Agency (EPA) Hazardous Waste Incinerator Regulations (40 CFR 264, Subpart O, Sections 264.340 - 264.351) require in Section 264.343(b) that

> "An incinerator burning hazardous waste and producing stack emissions of more than 1.8 kilograms per hour (4 pounds per hour) of hydrogen chloride (HCl) must control HCl emissions such that the rate of emission is no greater than the larger of either 1.8 kilograms per hour or 1% of the HCl in the stack gas prior to entering any pollution control equipment."

The regulations indicate that the affected incinerator facilities would need to monitor HCl on a continuous basis to economically demonstrate continuous compliance with the HCl emissions requirement of Section 264.343(b). Already, California and certain northeastern states (e.g. Connecticut, Massachusetts, New York, New Jersey, and Pennsylvania) now require that operating permits for new or proposed refuse-fired boilers include the provision that HCl continuous emission monitors (CEMs) will be installed and operated to demonstrate HCl removal requirements once HCl CEM systems are commercially available. However, the identification of the various types of commercially available HCl CEMS and the demonstration of their adequacy and effectiveness in continuously monitoring effluent HCl emissions from hazardous waste incinerators or refuse-fired boilers have not been documented.

The Quality Assurance Division (QAD) of EPA's Environmental Monitoring Systems Laboratory (EMSL), Research Triangle Park, North Carolina, has responsibility for assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support for other groups in the agency, including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Solid Waste. Accordingly, QAD requested that Entropy Environmentalists, Inc. conduct a laboratory and field project to evaluate the performance of commercially available HCl CEM instruments and systems.

The purpose of this project was to determine if commercially available equipment can be used to continuously monitor uncontrolled HCl emissions from municipal and hazardous waste combustion sources to demonstrate compliance with the Section 264.343(b) regulation. The major objectives of the project are (1) to evaluate the reliability of multiple HCl analyzers in terms of the accuracy, precision, and availability of measurement data, and (2) to determine the adequacy of several sampling systems for reliably providing effluent samples to the various HCl analyzers. Other objectives of this project included evaluation of (1) the stability of calibration gases, (2) alternate methods for calibrating the analyzers (wet-chemical standards, optical filters, etc.), and (3) wet-chemical sampling and analysis methods for use in assessing monitor performance relative to independent effluent measurements.

The HCl analyzers included in this evaluation were a Thermo Electron (TECO) Instruments Model 15; an MDA Scientific, Inc. Model 7100; a Lear Siegler Instruments (LSI)-owned CEA Instruments Model TGM-555; a Compur Model 4150 ZGSM; a CEA Instruments Model TGA 410; and a Bodenseewerk Spectran Model 677 IR. The project also included the evaluation of the Compur Model 4330 and TECO Model 200 dilution systems, the sampling system employed by the Bodenseewerk, and an extractive sampling system using a TECO Model 900 dilution system. The three analyzers that were not supplied with a probe and sample conditioning/handling system (i.e., the LSI, MDA, and CEA analyzers) were supplied gas samples from either the TECO or Compur dilution systems. Table 1-1 presents additional information pertaining to the analyzers and monitoring systems included in this evaluation.

A limited laboratory evaluation of the HCl analyzers and sample-handling systems was performed from May until November 1986 before the field-test phase of the program. The laboratory evaluation allowed Entropy personnel to become familiar with the operation and calibration techniques of four of the analyzers made available during that time. The HCl analyzers could not be subjected to some performance testing in the laboratory-phase evaluation because of delays in obtaining stable calibration gases.

The field-test phase of the monitor evaluation was conducted from November 1986 until May 1987 at a municipal refuse-fired boiler in Peekskill, New York. The source is not subject to HCl monitoring requirements or HCl emission control; the HCl effluent concentrations typically ranged between 200 and 500 ppm. The field evaluation included the concurrent operation of the various

TABLE 1-1. HCl CONTINUOUS EMISSION MONITORS

HCl Analyzer Make	Model	HCl Measurement Technique	Sampling System	Measurement Ranges	Available Calibration Techniques
Thermo Electron Instruments	15	NDIR gas filter correlation	Dilution system (dilution probe proposed)	Variable ranges from 0-5 ppm to 0-5000 ppm	Cylinder gases
MDA Scientific, Inc.	Series 7100	Dry reaction colorimetric	None	0-100 ppm or less	Stain card Cylinder gases
Lear Siegler Instruments	TGM-555	Wet-chemical colorimetric	None	0-50 ppm or less	Liquid standards Cylinder gases
Compur	4150	Ion-sensitive electrode	Dilution probe	0-3353 ppm	Liquid standards Cylinder gases
CEA Instruments*	TGA-410	Gas membrane galvanic cell	None	0-50 ppm or less	Liquid standards Cylinder gases
Bodenseewerk	677 IR	NDIR gas filter correlation (heated long-pathlength gas cell)	Heated probe, sampling line, and sampling pump to heated gas cell	0-1000 ppm	Cylinder gases Internal gas-filled cell

*CEA removed their analyzer from this evaluation in February 1987 because of the analyzer's inability to respond to changes in the gas sample.

analyzers and sampling systems to determine factors affecting the reliability of the equipment, calibration drift, calibration error, response time, and relative accuracy. The project will be continued at a later date at a combustion source that includes HCl emission control equipment.

This report presents findings and summarizes the results that were obtained from the project. Overall conclusions are presented in Section 2. Section 3 details the findings and results regarding various analyzer and monitoring system performances, the stability of HCl calibration gases, and comparison of wet-chemical analysis techniques. Section 4 presents a description of the facility and process where the field evaluation was conducted, as well as descriptions of the HCl monitoring equipment, setup of the equipment, and wet-chemical sampling and analysis procedures.

SECTION 2

CONCLUSIONS

The following conclusions are based on the results that were obtained from the project.

- Except for the CEA Model TGA-410, the HCl monitoring equipment produced effluent measurements that were in good agreement with concurrent wet-chemistry measurements for uncontrolled HCl emissions from a municipal waste combustion source.

- The TECO 200 and Compur sampling systems (which employ dilution probes), as well as the Bodenseewerk monitoring system (which uses a nondilution, heat-traced sampling system) can reliably provide representative effluent samples to the analyzers. The relative accuracy results indicate that the effect of HCl line losses can be minimized by injecting the HCl calibration gases through the entire sampling system when performing the dynamic calibrations.

- The gas vendor will change the HCl calibration gas cylinder valves to improve the ability in obtaining a representative sample from the cylinders.

- Relatively stable calibration cylinder gases are available at concentrations greater than 500 ppm.

- A dilution probe sampling system located upstream of particulate control equipment can deliver representative effluent samples to the analyzer.

- Operational problems were experienced with the Compur and MDA analyzers that were not apparent in performance test results.

- For some of the analyzers, the calibration gas injections and the relative accuracy tests do not always provide the same indication of CEM performance.

- The relative accuracy test data do not indicate biases for any of the monitor measurement techniques because of analytical interferences present in the effluent of this municipal boiler.

- The TECO 900 dilution unit does not extract and deliver a representative HCl gas sample to an analyzer within a one hour time period. The slow response time is apparently caused by adsorption effects in the sampling system at the less than 1 lpm sampling rate.

SECTION 3

DISCUSSION OF RESULTS

This section provides a summary and discussion of results obtained from the performance testing conducted during 1987 for the field evaluation. The impinger sample data afforded by ion chromatography (IC) analysis were used to perform all computations and to obtain all analytical results involving wet-chemical data.

Operational problems were experienced at the start-up of the analyzers and monitoring systems. Entropy personnel and the equipment vendors spent the first few months of the field evaluation identifying and resolving problems affecting the reliability of HCl monitor operation. A few problems were encountered that were not resolved.

The CEA Model TGA-410 HCl analyzer initially provided for the field evaluation did not respond to changes in sample concentration. CEA representatives suspected a bad electrochemical gas sensor within the analyzer and replaced the analyzer. However, the new analyzer performed similarly to the one it replaced. CEA thus withdrew its analyzer from the evaluation in February 1987.

The TECO 900 dilution unit could not deliver a sufficient amount of diluted sample flow to more than one HCl analyzer. When tested, the flow rate delivered by the TECO 900 dilution unit was 1 L/min. The rate should be approximately 3.5 L/min. The reduced sample flow might have been caused by the single-head sample pump contained within the TECO 900 unit which was not powerful enough to extract a sample from a negative pressure (-5 in. H_2O) sample location through 100 ft of heated, 0.25-in I.D. sample transport tubing. The TECO Model 15 analyzer response to diluted flue gas samples delivered by the TECO 900 dilution unit was zero. The zero response observed on the TECO 15 analyzer may have been caused by adsorption effects in the transport tubing and/or the TECO 900 dilution unit; the low sample flow rate may have been a contributing factor in the possible conditioning of the system. Also, even though the TECO 900 system sampled flue gas for approximately one hour without any response noted on the TECO 15 analyzer, more time may be required to properly condition the TECO 900 sampling system before it delivers a representative sample. Nevertheless, the TECO 900 dilution unit

was removed from this evaluation in January 1987 and may be further evaluated at a later date.

Monitor vendors were allowed to resolve any operational problems that were encountered with their equipment before the performance testing was initiated in March 1987.

3.1 RELATIVE ACCURACY DETERMINATIONS

In general, the results indicate acceptable HCl CEM performance during the relative accuracy test periods. Wet-chemical impinger sampling was conducted to collect "reference" HCl concentration measurements to compare to the HCl monitoring measurements so that relative accuracy could be determined. The computations of relative accuracy were performed using the procedures in Performance Specification 2, 40 CFR 60, Appendix A. A relative accuracy specification of $\leq$ 20% was adopted for this evaluation. CEM wet-basis measurement data were corrected to dry-basis so that a direct comparison could be made to the dry-basis impinger results.

Two relative accuracy tests were conducted in March and then repeated in April 1987. The relative accuracies of the TECO, MDA, and LSI analyzers were determined for samples provided by the Compur sampling system (March 19 and April 29) and for samples provided by the TECO model 200 sampling system (March 20 and April 27). The Compur and Bodenseewerk analyzers received all samples from their respective sampling systems. Tables 3.1 through 3.4 present the relative accuracy results for each of the CEMs. The calibration drift results, determined by injecting calibration gases before and after the testing, are presented at the bottom of the tables. The analyzers were operated continuously between the dates of the March and April relative accuracy tests. Hourly average effluent measurements were recorded for each analyzer. (See Appendix A for graphic presentations of relative accuracy data. The wet-chemical sampling data used in the relative accuracy computations are presented as tables in Appendix B.)

For the two March relative accuracy tests, duplicate wet-chemical samples were obtained at both the duct sampling location and the diluted sample manifold location to minimize the impact of imprecision in the wet-chemical sampling method. Very good agreement was observed between the duplicate sample

TABLE 3.1 RELATIVE ACCURACY DETERMINATION RESULTS (ppm HCl, Dry).
WESTCHESTER RESCO UNIT 2 - PEEKSKILL, NEW YORK, MARCH 19, 1987

Run No.	Duct Impinger Samples	Manifold Impinger Samples	HCl CEM Readings					Differences CEM Minus Duct Samples					Differences CEM Minus Manifold Samples				
			LSI*	BSWK	TECO*	MDA*	Compur*	LSI	BSWK	TECO	MDA	Compur	LSI	BSWK**	TECO	MDA	Compur
1	162	141	198	174	149	130	163	36	12	-13	-32	1	57	33	8	-11	22
2	394	343	388	442	370	312	364	- 6	48	-24	-82	-30	45	99	27	-31	21
3	365	291	351	388	331	279	326	-14	23	-34	-86	-39	60	97	40	-12	35
4	336	268	342	348	296	241	292	6	12	-40	-95	-44	74	80	28	-27	24
5	348	273	346	354	314	257	306	- 2	6	-34	-91	-42	73	81	41	-16	33
6	364	301	370	386	336	263	319	6	22	-28	-101	-45	69	85	35	-38	18
7	358	291	348	365	322	256	303	-10	7	-36	-102	-55	57	74	31	-35	12
8	397	338	394	412	380	332	363	- 3	15	-17	-65	-34	56	74	42	- 6	25
9	401	315	382	407	373	313	356	-19	6	-28	-88	-45	67	92	58	- 2	41
10	337	291	357	365	346	278	329	20	28	9	-59	- 8	66	74	55	-13	38
11	361	291	360	364	334	268	315	- 1	3	-27	-93	-46	69	73	43	-23	24
12	367	310	397	411	380	281	343	30	44	13	-86	-24	87	101	70	-29	33
	Mean 349	Mean 288	Mean Differences (ppm) =					3.6	18.8	-21.6	-81.7	-34.2	65.0	80.3	39.8	-20.3	27.2
			Confidence Intervals (ppm) =					10.9	9.4	10.8	12.9	10.5	6.9	11.5	10.3	7.5	5.6
			Relative Accuracy(%) =					4.2	8.1	9.3	27.1	12.8	25.0	31.9	17.4	9.7	11.4

* Compur sampling system (40:1 dilution)

**The comparison of the Bodenseewerk values to the manifold impinger samples is presented only to indicate the relative difference between the two sets of impinger samples

CALIBRATION DRIFT RESULTS

	LSI	Bodenseewerk	TECO	MDA	COMPUR
Pre-test calibration					
Zero	12 ppm	---	5 ppm	1 ppm	30 ppm
479 ppm HCl	478 ppm	---	493 ppm	471 ppm	502 ppm
Post-test calibration					
Zero	15 ppm	- 3 ppm	27 ppm	0 ppm	31 ppm
479 ppm HCl	494 ppm	470 ppm	532 ppm	562 ppm	492 ppm
Calibration Drift					
Zero	0.2%	---	0.6%	0%	0%
Upscale	0.8%	---	1.0%	2.3%	-0.3%

TABLE 3.2 RELATIVE ACCURACY DETERMINATION RESULTS (ppm HCl, Dry).
WESTCHESTER RESCO UNIT 2 - PEEKSKILL, NEW YORK, MARCH 20, 1987

Run No.	Duct Impinger Samples	Manifold Impinger Samples	HCl CEM Readings					Differences CEM Minus Duct Samples					Differences CEM Minus Manifold Samples				
			LSI*	BSWK	TECO*	MDA*	Compur*	LSI	BSWK	TECO	MDA	Compur	LSI	BSWK**	TECO	MDA	Compur
13	370	317	410	402	414	355	343	40	32	44	-15	-27	93	85	97	38	26
14	354	328	431	430	452	367	375	78	77	99	14	22	103	102	124	39	47
15	409	343	444	443	488	392	382	36	35	80	-16	-26	101	100	145	49	39
16	329	281	388	357	417	351	325	59	28	88	22	- 4	107	76	136	70	44
17	216	203	275	239	305	238	227	58	22	88	21	10	72	36	102	35	24
18	285	255	347	302	380	281	290	63	18	96	- 3	6	92	47	125	26	35
19	321	265	389	339	410	290	318	68	18	89	-31	- 3	124	74	145	25	53
20	353	286	411	375	448	319	375	58	22	95	-34	22	125	89	162	33	89
21	237	187	332	241	324	247	286	95	4	87	10	49	145	54	137	60	99
	Mean 319	Mean 274	Mean Differences (ppm) =					61.7	28.4	85.1	- 3.6	5.4	106.9	73.7	130.3	41.7	50.7
			Confidence Intervals (ppm) =					13.8	15.6	12.6	16.6	18.6	16.7	18.0	16.1	11.7	20.3
			Relative Accuracy (%) =					23.7	13.8	30.6	6.3	7.5	45.1	33.5	53.4	19.5	25.9

* TECO sampling system (45:1 dilution)
**The comparison of the Bodenseewerk values to the manifold impinger samples is presented only to indicate the relative difference between the two sets of impinger samples

CALIBRATION DRIFT RESULTS

	LSI	Bodenseewerk	TECO	MDA	COMPUR
Pre-test calibration					
Zero	1 ppm	---	3 ppm	1 ppm	25 ppm
479 ppm HCl	484 ppm	---	477 ppm	522 ppm	474 ppm
Post-test calibration					
Zero	10 ppm	---	15 ppm	1 ppm	29 ppm
479 ppm HCl	475 ppm	---	561 ppm	542 ppm	522 ppm
Calibration Drift					
Zero	0.4%	---	0.3%	0%	0.1%
Upscale	-0.4%	---	1.9%	0.4%	1.4%

TABLE 3.3 RELATIVE ACCURACY DETERMINATION RESULTS (ppm HCl, Dry).
WESTCHESTER RESCO UNIT 2 - PEEKSKILL, NEW YORK, APRIL 27, 1987

Run No.	Duct Impinger Samples	Manifold Impinger Samples	HCl CEM Readings					Differences CEM Minus Duct Samples					Differences CEM Minus Manifold Samples				
			LSI*	BSWK	TECO*	MDA*	Compur*	LSI	BSWK	TECO	MDA	Compur	LSI	BSWK**	TECO	MDA	Compur
1	511	456	538	525	539	450	390	27	14	28	-61	-121	82	69	83	- 6	- 66
2	475	525	549	496	571	477	381	74	21	96	2	- 94	24	-29	46	-48	-144
3	510	535	564	516	601	509	391	54	6	91	- 1	-119	29	-19	66	-26	-144
4	409	413	476	420	473	418	323	67	11	64	9	- 86	63	7	60	5	- 90
5	401	419	456	420	467	393	324	55	19	66	- 8	- 77	37	1	48	-26	- 95
6	394	413	473	419	469	407	330	79	25	75	13	- 64	60	6	56	- 6	- 83
7	361	376	439	385	430	375	305	78	24	69	14	- 56	63	9	54	- 1	- 71
8	390	387	437	---	448	382	322	47	--	58	- 8	- 68	50	---	61	- 5	- 65
9	394	398	459	421	456	403	323	65	27	62	9	- 71	61	23	58	5	- 75
10	451	477	505	483	517	463	389	54	32	66	12	- 62	28	6	40	-14	- 88
	Mean 430	Mean 440	Mean Differences (ppm) =					60	19.9	67.5	-1.9	-81.8	49.7	8.1	57.2	-12.2	-92.1
			Confidence Intervals (ppm) =					11.5	6.4	13.3	16.0	16.5	13.8	21.2	8.5	11.9	20.9
			Relative Accuracy (%) =					16.6	6.1	18.8	4.2	22.9	14.4	6.6	14.9	5.5	25.7

* TECO sampling system (45:1 dilution)

**The comparison of the Bodenseewerk values to the manifold impinger samples is presented only to indicate the relative difference between the two sets of impinger samples

CALIBRATION DRIFT RESPONSE

	LSI	Boden-seewerk	TECO	MDA	COMPUR
Pre-test calibration					
Zero	0 ppm	---	0 ppm	3 ppm	18 ppm
503 ppm HCl	505 ppm	---	500 ppm	498 ppm	500 ppm
Post-test calibration					
Zero	7 ppm	---	24 ppm	3 ppm	28 ppm
503 ppm HCl	484 ppm	---	508 ppm	516 ppm	535 ppm
Calibration Drift					
Zero	0.3%	---	0.5%	0%	0.3%
Upscale	-0.9%	---	0.2%	0.4%	1.0%

TABLE 3.4 RELATIVE ACCURACY DETERMINATION RESULTS (ppm HCl, Dry).
WESTCHESTER RESCO UNIT 2 - PEEKSKILL, NEW YORK, APRIL 29, 1987

Run No.	Duct Impinger Samples	Manifold Impinger Samples	HCl CEM Readings					Differences CEM Minus Duct Samples					Differences CEM Minus Manifold Samples				
			LSI*	BSWK	TECO*	MDA*	Compur*	LSI	BSWK	TECO	MDA	Compur	LSI	BSWK**	TECO	MDA	Compur
11	320	306	358	332	329	293	287	38	12	9	-27	-33	52	26	23	-13	-19
12	338	301	349	332	332	297	296	11	- 6	-6	-41	-42	48	31	31	- 4	- 5
13	358	343	389	372	373	333	342	31	14	15	-25	-16	46	29	30	-10	- 1
14	339	329	355	345	347	319	318	16	6	8	-20	-21	26	16	18	-10	-11
15	351	315	361	353	354	329	321	10	2	3	-22	-30	46	38	39	14	6
16	351	273	371	341	349	338	314	20	-10	-2	-13	-37	98	68	76	65	41
17	333	287	344	343	349	335	299	11	10	16	2	-34	57	56	62	48	12
18	363	310	364	372	375	359	---	1	9	12	- 4	---	54	62	65	49	---
19	306	254	333	314	324	316	315	27	8	18	10	9	79	60	70	62	61
20	357	296	357	366	367	362	357	0	9	10	5	0	61	70	71	66	61
	Mean 342	Mean 301	Mean Differences (ppm) =					16.5	5.4	8.3	-13.5	-22.7	56.7	45.6	48.5	26.7	16.1
			Confidence Intervals (ppm) =					9.0	5.6	5.6	11.7	13.4	14.1	14.1	16.0	24.5	23.5
			Relative Accuracy (%) =					7.5	3.2	4.1	7.4	10.6	23.5	19.8	21.4	17.0	13.2

Runs 11-15 (2 lpm impinger sampling rate)					
MD	43.6	28.0	28.2	- 4.6	-6.0
CI	12.6	10.0	10.0	13.5	11.8
RA	17.6	11.9	12.0	5.7	5.6
Runs 16-20 (1 lpm impinger sampling rate)					
MD	69.8	63.2	68.8	58.0	43.8
CI	23.0	7.2	6.8	10.9	36.9
RA	32.7	24.8	26.6	24.3	29.0

* Compur sampling system (40:1 dilution)

**The comparison of the Bodenseewerk values to the manifold impinger samples is presented only to indicate the relative difference between the two sets of impinger samples

CALIBRATION DRIFT RESULTS

	LSI	Boden-seewerk	TECO	MDA	COMPUR
Pre-test calibration					
Zero	0 ppm	---	0 ppm	2 ppm	17 ppm
503 ppm HCl	508 ppm	---	496 ppm	508 ppm	490 ppm
Post-test calibration					
Zero	-7 ppm	---	21 ppm	3 ppm	28 ppm
503 ppm HCl	466 ppm	---	500 ppm	655 ppm	529 ppm
Calibration Drift					
Zero	-0.4%	---	0.5%	0%	0.2%
Upscale	-2.2%	---	0.1%	3.7%	1.2%

results. Accordingly, only single samples were collected at each location for the April relative accuracy tests. The wet-chemical impinger sampling and analysis procedures are presented in Section 4.3.

Before the start of each relative accuracy test, each analyzer was calibrated with the same HCl calibration gas. Because of the close agreement between the Bodenseewerk response to calibration gas and its response to the analyzer's internal gas-filled cell, calibration gas was injected through the Bodenseewerk monitoring system only periodically to conserve calibration gas.

The response time for each analyzer and monitoring system was determined, but it was not accounted for in the interpretation of recorded data. The CEMSs sampled flue gas for 30 minutes before the start of any relative accuracy test. The relative accuracy determinations comparing the manifold impinger samples to the CEM measurements are not impressive. Apparently these manifold impinger results are affected by any HCl loss within the system, whereas any possible HCl loss has been calibrated out of the analyzer measurements (see Section 3.5). The difference between the two sets of mean difference terms (CEM-manifold impinger sample difference vs. CEM-duct impinger sample difference) reflects the compensation in analyzer calibration for HCl loss in the sampling system. The relative accuracy results using the manifold samples would be applicable only if the analyzers were calibrated by injecting the calibration gas directly into the analyzers, and not through the entire sampling system; thus any bias due to line loss would have the same impact on both results.

Other findings that resulted from the relative accuracy determinations are briefly described below:

- The Bodenseewerk monitoring system demonstrated the most consistent behavior during the four relative accuracy tests and was the only analyzer/monitoring system to produce results that were all within the adopted $\leq$20% specification.

- The results of the calibration checks did not always provide an indication of monitor performance during the relative accuracy tests. In each of the four cases where the relative accuracy result exceeded the $\leq$20% specification, the magnitude of the mean difference term indicated the reason for exceeding the specification may have been miscalibration. In two of these four cases, there was good agreement between the calibration gas values and the CEM responses to the calibration gas injections. In one case, the calibration check results were not consistent with the relative accuracy mean difference term (i.e., positive drift was noted from the post-test calibration check, but the relative accuracy mean difference term indicated a negative bias in the flue gas measurement). On one occasion, a significant

amount of drift was noted (3.7% relative to instrument span, or 29% relative to the pre-test response), whereas the relative accuracy result (7.4%) indicated acceptable monitor performance.

- The relative accuracy results indicate that any effects of HCl line losses can be minimized by injecting the HCl calibration gases through the entire sampling system when performing dynamic calibrations.

- During the final relative accuracy test conducted on April 29, 1987, the sampling rate for the last five manifold impinger samples was reduced from 2 L/min (the prescribed sampling rate) to 1 L/min to determine if the sample flow rate had an effect on the results. Significantly lower impinger sample results were produced at the lower sampling rate (see Table 3.4). The stainless steel hardware mounted on the manifold could possibly have contributed to these lower impinger sample values by adsorbing HCl at the lower flow rate.

3.2 CALIBRATION DRIFT DETERMINATION

A 7-day calibration drift evaluation was not performed according to the procedures of promulgated Performance Specification 2, Federal Register, Volume 48, No. 102, May 25, 1983, page 23608. However, calibration checks were performed daily over 3- and 4-day periods according to the calibration drift test procedures. These data were compiled to demonstrate the capabilities of these HCl analyzers to maintain daily drift within the 2.5% of span specification of Performance Specification 2 adopted for this evaluation.

Table 3.5 presents the maximum daily calibration drift observed for each of the analyzers. The calibration drift work sheets are located in Appendix C.

The calibration drift test was conducted on the Bodenseewerk monitoring system for seven consecutive days by using the data afforded by the automatic calibration check the Bodenseewerk performs using zero air and the internal gas-filled cell. This procedure did not require test personnel to remain on-site for seven consecutive days.

TABLE 3.5. SUMMARY OF MAXIMUM DAILY CALIBRATION DRIFT*

Analyzer	Low Range	High Range
LSI	2.2% (0/14)	4.2% (1/14)
Bodenseewerk	0.3% (0/10)	0.7% (0/10)
TECO	1.3% (0/15)	1.4% (0/15)
MDA	0.1% (0/15)	9.9% (9/15)
Compur	2.7% (1/10)	4.7% (2/10)

*Numbers in parantheses are number of days on which the drift exceeded the 2.5% specification/number of test days.

The data presented on the calibration drift work sheets indicate the MDA and Compur analyzers may have difficulty producing repeatable results to satisfy the adopted calibration drift requirement. The problems associated with analyzer performance are addressed in Section 3.6.

3.3 CALIBRATION ERROR DETERMINATION

Calibration error determinations were performed on four of the five monitors. The Bodenseewerk monitoring system did not undergo a calibration error test because only one of the HCl calibration gases (the 503 ppm cylinder gas) was within the 0-1000 ppm operating range of the analyzer. The Bodenseewerk does not use a dilution device, as do the Compur and TECO sampling systems. Periodic injections of the single gas yielded responses that were in excellent agreement with the gas value.

Two sets of calibration error determinations were performed, one each for the TECO and Compur sample-handling systems. The monitors were initially calibrated to the 503 ppm HCl calibration gas by flowing the gas through the entire sampling system. The 503 ppm gas provided a calibration point in the range of expected HCl emissions at this particular source.

The calibration error test procedure involved performing five nonconsecutive injections of the zero air and two HCl calibration gases through the entire monitoring system. The differences between the monitor responses and the known concentrations of the calibration gases were recorded. The calibration error determinations were computed by summing the absolute value of the mean difference and the 95% confidence interval determined for the five injections.

Table 3.6 presents a comparison of the monitor calibration error determinations conducted on the two sampling systems. The calibration error work sheets are located in Appendix D of this report.

The following observations can be made from the results:

- Most of the calibration error results exceeded the $\leq 5\%$ specification adopted for this evaluation. All the CEM responses to the 503 ppm gas, except for one MDA response, were within $\pm 8\%$ of the cylinder gas value. For comparison purposes, all the monitors produced responses to the 503 ppm gas injections that would meet the Appendix F, Procedure 1 acceptable accuracy requirement of $\pm 15\%$ using the Cylinder Gas Audit (CGA) procedure. The CGA procedure requires three gas injections of each of two audit gases and specifies that the average of the three responses should be used in determining accuracy. Monitor imprecision is not accounted for because the confidence interval is not included in the Procedure 1 accuracy determination.

- Consistent performance of the TECO and MDA monitors was observed on both the Compur and TECO sampling systems.

- Because the LSI and MDA analyzers were calibrated to the 503 ppm HCl calibration gas, the LSI and MDA results for the high-level check (1556 ppm) are excessive as a result of the nonlinearity associated with the measurement techniques of these two monitors.

- The magnitude of the confidence interval terms for some of the analyzers reflects a high degree of monitor imprecision during these tests. These analyzers had difficulty producing repeatable responses to the same calibration gas. This same problem also affected the daily calibration drift results.

TABLE 3.6. SUMMARY OF CALIBRATION ERROR TESTS, APRIL 22, 1987

Analyzer	Calibration Error* Mid-level (503 ppm)	High-level (1556 ppm)
Compur Sampling System (40:1 dilution)		
LSI	(+) 3.5%	(+) 37.7%
TECO	(+) 7.9%	(-) 2.3%
MDA	(+) 13.9%	(-) 16.3%
Compur	(+) 7.0%	(+) 10.2%
TECO Sampling System (45:1 dilution)		
LSI+	----	----
TECO	(+) 3.4%	(-) 8.1%
MDA	(+) 8.6%	(-) 21.7%

*The sign within parentheses denotes whether the mean of the monitor responses was greater than (+) or less than (-) the known concentration of the injected calibration gas.

+Not tested on TECO sampling system because of the long response time of the analyzer and also the shortage of available calibration gas.

3.4 RESPONSE TIME

The response time is defined as the amount of time required for the measurement system to display 95% of a step change in gas concentration on a

data recorder. The response times were determined by injecting zero air and HCl calibration gases through the entire monitoring system. The response times of the LSI, TECO, and MDA analyzers were determined first for samples delivered by the Compur sampling system, and then for samples provided by the TECO sampling system. The results are presented in Table 3.7.

The TECO and Compur sampling system response times were checked by using a CO analyzer and CO calibration gases. Each sampling system provided a representative CO calibration gas sample to the CO analyzer in less than 1 min. The slower response times when zero air and HCl calibration gas were used may be due not only to the analyzer response time, but also to conditioning of the sampling system.

TABLE 3.7 SUMMARY OF RESPONSE TIMES TO HCl GAS INJECTIONS

System	Response Times (min)
Bodenseewerk Monitoring System	3
Compur Monitoring System	5
Compur Sampling System	
LSI	15
TECO	4
MDA	4
TECO Sampling System	
LSI	16
TECO	5
MDA	6

3.5 COMPARISON OF THE TECO MODEL 200 AND COMPUR MODEL 4330 SAMPLING SYSTEMS

The results afforded by the various performance tests that were conducted on both sampling systems indicate no significant difference in the ability of either sampling system to deliver a representative sample to an HCl CEM.

The primary physical differences between these two similar sampling systems are that (1) the Compur dilution probe sample critical orifice is constructed of stainless steel and is electrically heated to maintain a constant

temperature, whereas the TECO dilution probe critical orifice is constructed of glass and is not heated except by the flue gas; and (2) the Compur system delivers diluted sample flow to the CEMs at a rate of approximately 33 L/min, whereas the TECO system delivers sample at approximately 6 L/min.

Figures 3-1, 3-2, and 3-3 graphically present a comparison between the manifold and duct wet-chemical impinger sample data. These samples were collected simultaneously at both locations (described in Section 4.4) during relative accuracy testing to evaluate the performance of each sample handling system. The data indicate that in both tests involving the Compur sampling system, and in one of the two tests involving the TECO Model 200 system, one of the following events had occurred: (1) the dilution ratios of the two dilution probes had changed, and thus an incorrect dilution factor was used to correct the diluted manifold values to represent actual flue gas concentrations, or (2) some HCl was lost through the sampling system.

The dilution ratios of both probes were checked periodically by using a CO analyzer and CO calibration gases. The dilution ratio never changed without indicating a significant change in either the sample orifice vacuum or the dilution air delivery pressure. The dilution ratios were also verified immediately before the initiation of each of the four relative accuracy tests.

Therefore, it can be assumed that the differences noted during three of the four relative accuracy test periods are due to HCl loss in the sampling system. Both sampling systems transport the diluted flue gas sample at relatively high flow rates through heat-traced tubing ($300^{o}F$). "Memory effects" (HCl losses due to wall adsorption of HCl) are less likely to occur under these conditions. The apparent difference between the duct and manifold sample results may be attributed to HCl loss to the stainless-steel components on the manifold, which included a few type 316 stainless-steel fittings and ball valves. The sample delivered by either sampling system to the common glass manifold passed through the stainless-steel hardware before it entered the HCl impinger train. Therefore, because of the potential for HCl loss, the use of stainless-steel components was minimized wherever possible.

As previously discussed, HCl loss in the sampling system should not be a concern as long as the loss is not severe and the effects are minimized by flowing HCl calibration gas through the entire system during calibrations of the monitoring system.

HCl IMPINGER SAMPLE COMPARISON

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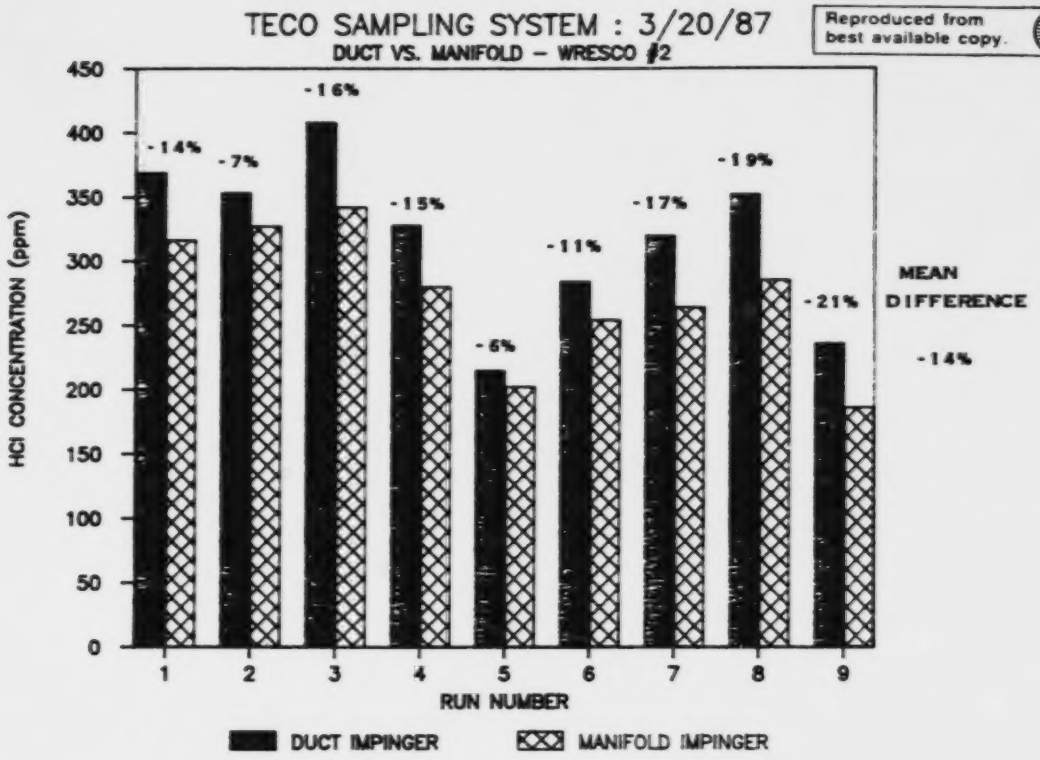


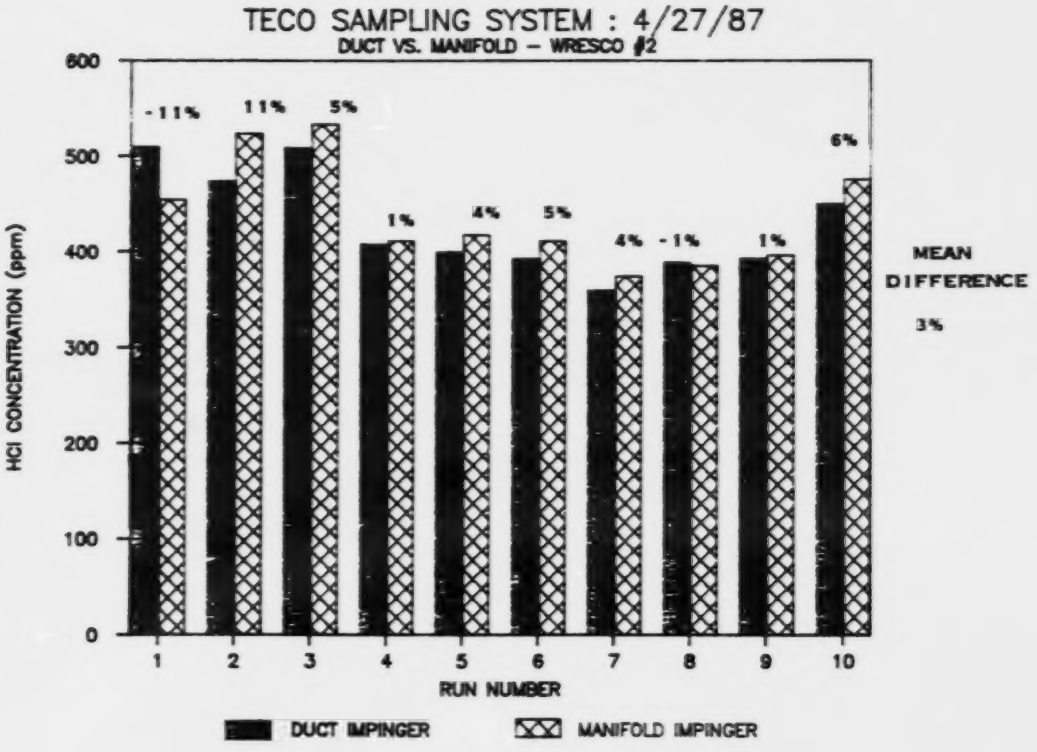
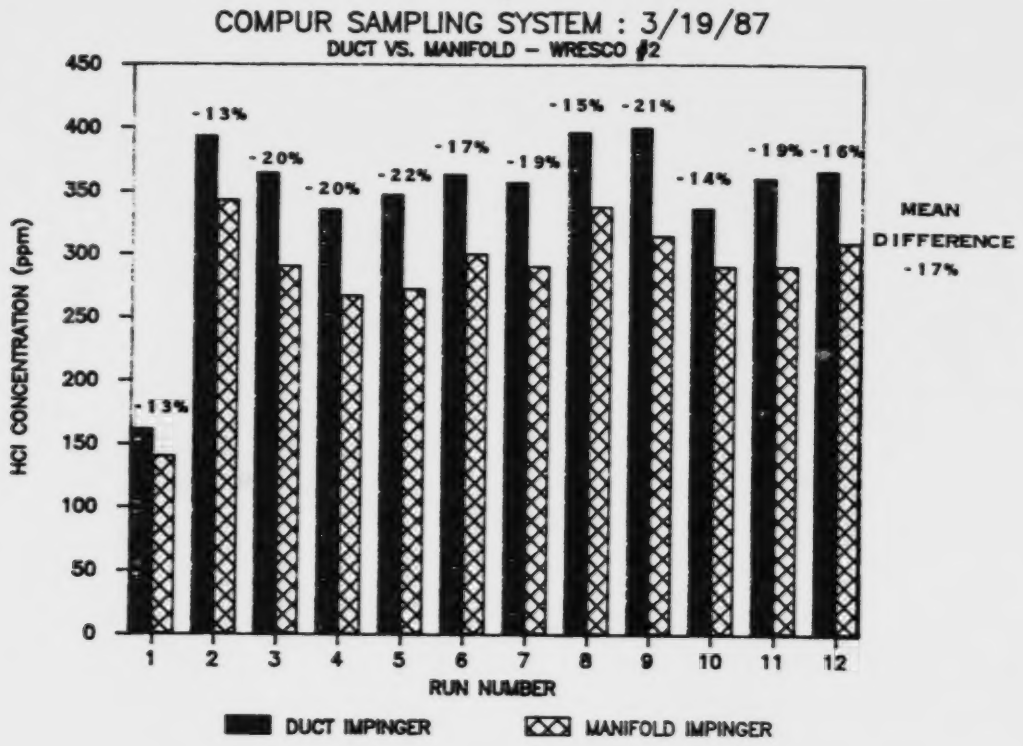


Figure 3-1.

HCl IMPINGER SAMPLE COMPARISON



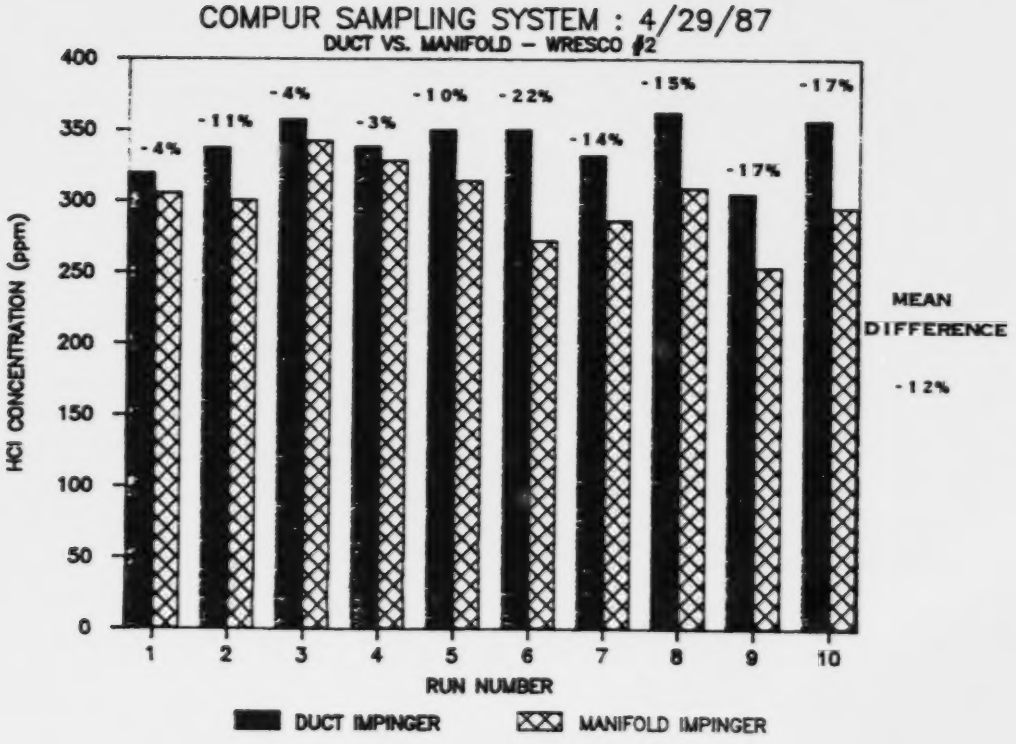


FIGURE 3-2.

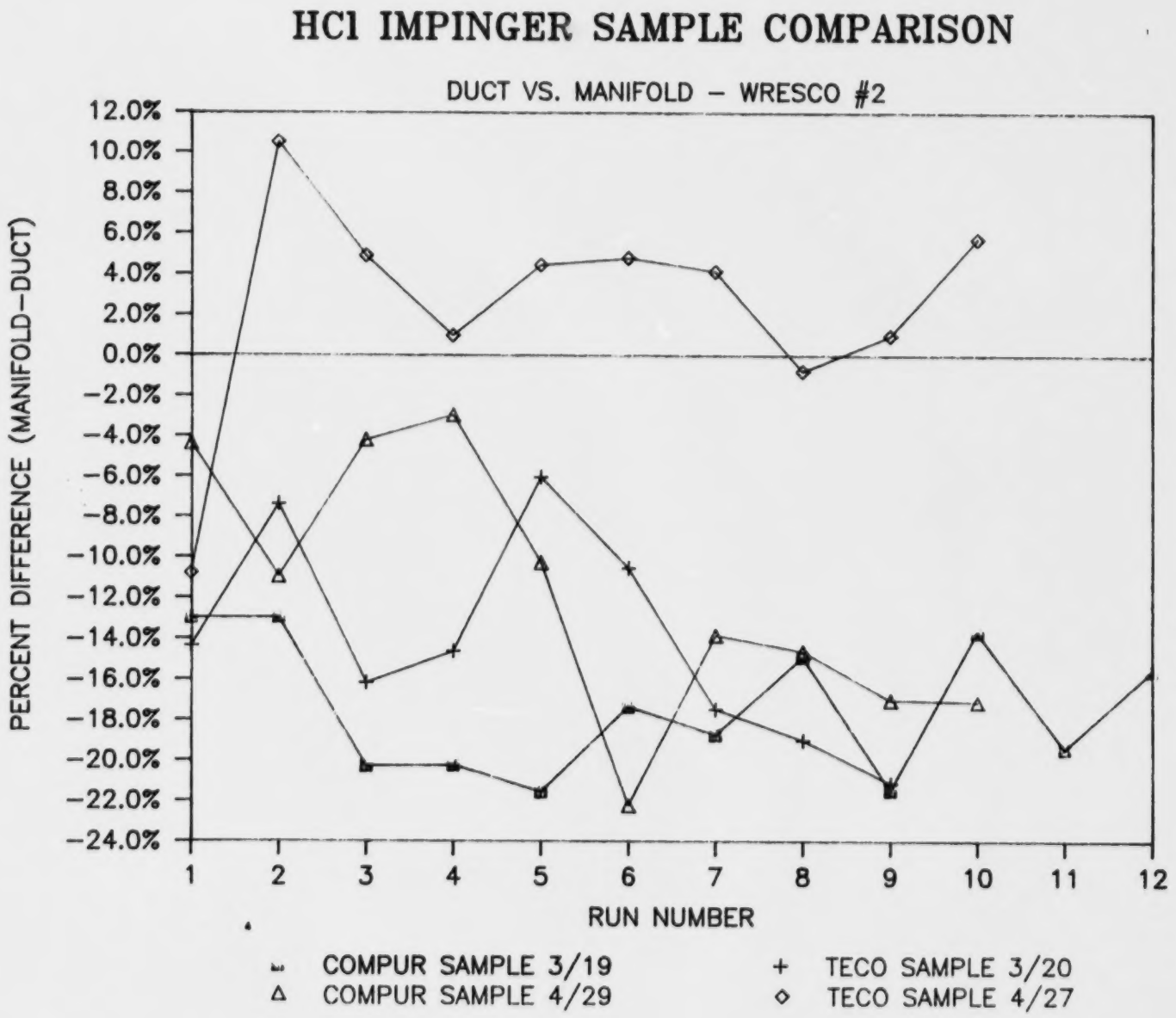

HCl IMPINGER SAMPLE COMPARISON
DUCT VS. MANIFOLD – WRESCO #2
PERCENT DIFFERENCE (MANIFOLD–DUCT)
12.0%
10.0%
8.0%
6.0%
4.0%
2.0%
0.0%
−2.0%
−4.0%
−6.0%
−8.0%
−10.0%
−12.0%
−14.0%
−16.0%
−18.0%
−20.0%
−22.0%
−24.0%
1
2
3
4
5
6
7
8
9
10
11
12
RUN NUMBER
COMPUR SAMPLE 3/19
COMPUR SAMPLE 4/29
TECO SAMPLE 3/20
TECO SAMPLE 4/27

FIGURE 3-3.

3.6 OPERATING PROBLEMS

This section summarizes the operational problems encountered during the field evaluation.

3.6.1 LSI/CEA TGM-555 Analyzer

Routine maintenance was the only attention required by the analyzer and included the following: (1) once a month, clean the glass sample and reference cells, as well as the internal plumbing that transports the reagents; (2) check the analyzer's internal vacuum pump flow rate weekly; and (3) replenish the 4-L supply of each reagent weekly.

The response time of the analyzer is the slowest of all the analyzers in the program. The analyzer takes approximately 10 min to achieve a stable response to an upscale gas from a zero condition. The slow calibration of the analyzer requires longer calibration gas injections, which requires considerably more gas.

The analyzer measurement output is nonlinear; however, the calibration and flue gas measurements are in the range of 15% - 30% of the operating range of the analyzer. The calibration curve is relatively linear in this range.

3.6.2 TECO 15 Analyzer/200 Dilution System

The zero drift problem experienced early in the program was not caused by a leak in the gas filter correlation wheel as suspected. Dust from inside the trailer was passing through the analyzer cabinet filter and accumulating on the surface of the wheel, which subsequently caused the gradual zero drift in the positive direction. Cleaning the gas filter correlation wheel with deionized water bimonthly reduced the drift to an acceptable level.

3.6.3 MDA 7100 Analyzer

A discrepancy exists between the calibration curves generated by the two available calibration techniques: (1) optics (stain card), which only checks the electronics, and (2) the dynamic calibration. MDA may have used an unstable HCl calibration gas to perform the original dynamic gas calibration. This dynamic calibration is performed at the time of manufacture and is used to name the stain card values.

Wet-chemical results have indicated that a positive bias is introduced in the MDA measurements when the instrument is calibrated only with the stain card. An optics and dynamic calibration both were performed prior to all performance tests.

Occasionally, Entropy performed consecutive optics and dynamic calibrations and observed poor repeatability in the calibration factors produced by these calibrations. Three consecutive optics calibrations were performed on April 7, 1987, which resulted in the following Q calibration factors: 1.067, 0.865, and 0.986. Dynamic calibrations produced similar behavior. Dynamic calibrations using the same calibration gas were conducted from April 21 to April 29, 1987; the resultant K calibration factors ranged from 0.593 to 0.943. These Q and K calibration factors are multipliers and greatly affect the analyzer's measurements.

Figure 3-4 graphically illustrates the changes observed in the analyzer's calibration during a one-week period in January 1987. Both an optics and dynamic calibration were initially performed on January 23. On subsequent days, only the optics calibration was performed before to recording the analyzer's responses to calibration gas injections. The Q calibration factor is self-adjusting each time the optics calibration is performed using the "stain card," and serves as a method for automatic readjustment of the zero and span of the instrument.

Particles from the Chemcassette tape accumulated on the gate screen located in the analyzer's detection head. The gas sample is exposed to the Chemcassette tape and then drawn through the screen by an internal pump. After a few days of continuous operation, the gas sample flow through the analyzer was restricted because the screen had become plugged. Cleaning the screen was therefore performed biweekly. Maintaining the proper sample flow rate is critical to the HCl measurement.

3.6.4 Compur 4150 Analyzer/Compur 4330 Dilution System

Problems continued to plague the Compur analyzer. Compur service representatives visited the test site in January and again in March 1987 to resolve operational problems that had been enountered. Compur personnel attempted to resolve some of these problems by replacing the reagent pump with

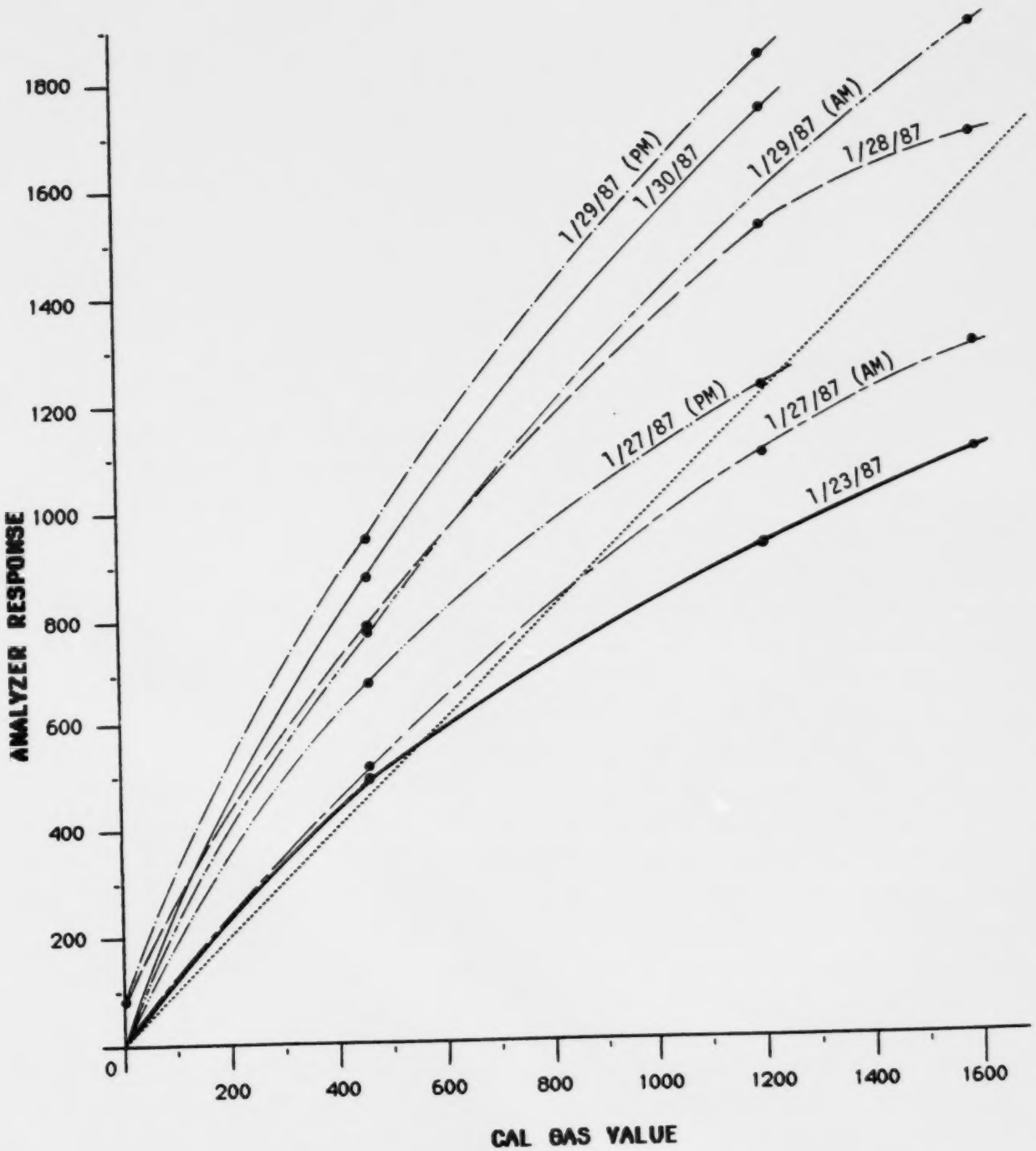


Figure 3-4. Changes in MDA 7100 analyzer calibration.

a peristaltic pump; they also replaced the entire measuring cell, which includes new reference and chloride ion electrodes and solution delivery system.

Erratic analyzer responses to the absorbing solution and liquid standard during automatic calibrations were observed on numerous occasions. The analyzer measurements of flue gas also gradually increased until the reading exceeded the operating range and generated a "System Fault - A/D Conversion Overflow" condition. These examples of analyzer behavior indicated a problem with the electrodes. When erratic behavior was observed, the positioning of the reference and chloride ion electrodes was adjusted to either increase or decrease the distance between the two electrodes' tips. In most cases, this arbitrary adjustment caused the analyzer readings to return to the expected values. Cleaning the electrodes was performed but did not help prevent this behavior from recurring.

The analyzer has no zero and span potentiometers to adjust for calibration adjustment. The only adjustments possible were to vary the gas sample flow rate and the reagent flow rate to the atomizer. These adjustments changed the enrichment factor and thus the HCl concentration in solution.

The Compur dilution probe critical orifice became plugged on two occasions. This condition was identified by the low analyzer responses to both flue gas and calibration gas samples. Quartz glass wool was placed in the probe tip upstream of the critical orifice to provide additional protection for the orifice. No further plugging was encountered.

A significant decrease in the effluent temperature (due to a unit outage or decrease in boiler load) caused the Compur probe to cool to below the lower temperature set point of the probe heater, which generated a fault condition with the system. Apparently, the probe heater could not maintain the prescribed 392°F temperature after the flue gas temperature cooled to less than 200°F. This fault condition occurring during a unit outage is not a concern; however, when the effluent temperature returned to the typical 400° - 450°F range, the probe temperature increased to the prescribed temperature and began delivering flue gas sample to the CEM. But the Compur analyzer remained in the fault mode because it can be returned to service only if the reset button on the analyzer is manually depressed.

3.7 CALIBRATION GAS STABILITY

Early in the program Scott Specialty Gases provided Entropy with HCl calibration gases contained within "conditioned" steel cylinders (Aculife V conditioning process). When attempting to determine the HCl concentrations of these cylinder gases, Entropy occasionally experienced problems in producing repeatable cylinder gas sampling and analysis results. The cause for the inconsistent results was suspected to be associated with sampling of the cylinder gas. The sampling was conducted by using a modified Method 6 train with 0.1 NaOH as the reagent (see Figure 3-5). At various time intervals, Entropy performed triplicate sampling and analyzed the samples on an ion chromatograph. Occasionally more than three sampling runs were performed on each of the cylinders. After eliminating outliers (individual results that were greater than 10% of the average of the sample results), Entropy concluded that stable HCl calibration gases were available. However, deterioration of the cylinder contents (possibly an exponential decay) should be expected, and analysis of the cylinder gases should be routinely conducted to verify the concentration.

Additional HCl calibration gases were purchased from Scott Specialty Gases, and sampling and analysis of the cylinder gases was conducted periodically to verify the concentration of each cylinder. The composite results of the cylinder gas analyses are presented in Table 3.8.

The results indicate that all the cylinder gases contained within conditioned cylinders are relatively stable; the variation between analysis results is attributed to possible problems in collecting representative samples. The cylinder with the 1696 ppm HCl tag value appears to be the only conditioned cylinder to exhibit any noticeable decay (11% after 6 months) on the basis of data collected to date.

One of the problems Entropy experienced in attempting to determine the HCl concentration of the cylinder gas was the occasional poor agreement between sample results from a single cylinder. The prevalent behavior observed was an increase in the HCl concentrations (to the expected values) with successive runs of the same cylinder gas sample. Conditioning of the sample delivery system (comprising 316 stainless-steel and Teflon components) was suspected to have caused this phenomenon. To eliminate or reduce this observed increase and any other possible deterrents in collecting a representative sample, Entropy

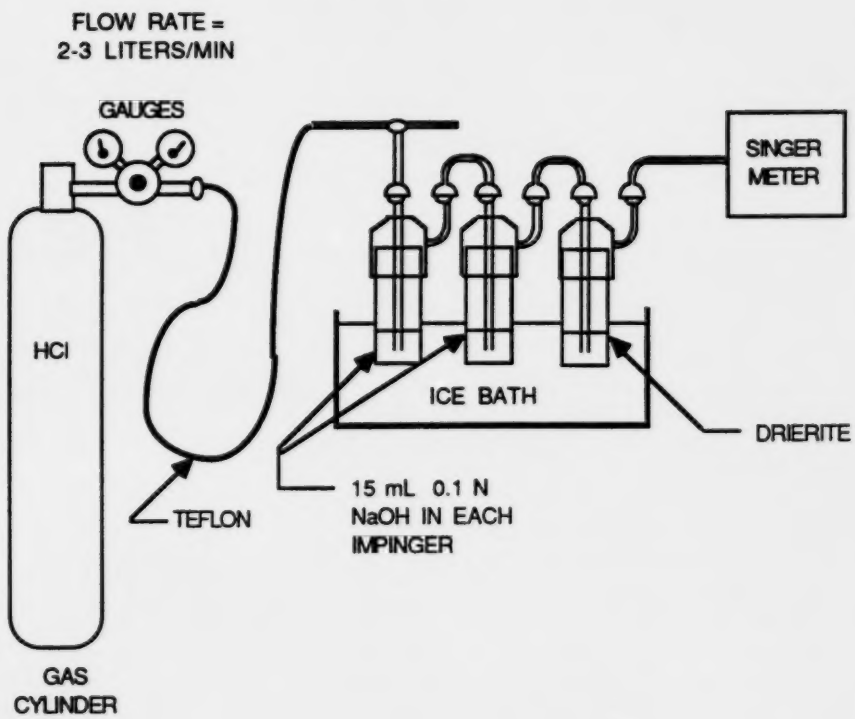


Figure 3-5. Cylinder gas sampling setup.

TABLE 3.8. HCl CYLINDER GAS ANALYSIS (ppm)

Tag Value	Cylinder No.	6/11/86	7/3/86	9/11/86	9/19/86	9/30/86	10/31/86	11/13/86	12/3/86	1/28/87*	4/1/87
Unconditioned Cylinders											
551	(B-1404)	385									
75	(B-882)	0									
10,000	(B-2345)	433	405								
1,590	(B-1572)	673					328		263		
Conditioned Cylinders											
1,696	(A-17241)			1716	1732	1668	1680	1647	1592	1572	1525
467	(A-16790)			431	456	473	414	462	414	406	439
1,175	(K-9368)								1281	1204	1222
479	(K-9370)								453	461	459
1,556	(K-9862)										1624
503	(K-9841)										498

* Titration analysis was used because integrator was unavailable for IC.

employed the following three practices in addition to the standard sampling procedures: (1) purge the delivery system connecting the gas cylinder to the impinger train with cylinder gas for 5 min before sampling the bottle, (2) maintain a sample flow rate greater than 1 L/min, and (3) keep the delivery system closed to ambient air when not sampling. Improved agreement between the sample results was observed during subsequent cylinder gas sample collections (namely, the calibration gas analyses conducted on 1/28/87 and 4/1/87).

At the conclusion of the field testing portion of this evaluation, Scott Specialty Gases informed Entropy of a finding that may also have affected the cylinder gas analysis results. The gas vendor discovered that sampling and analysis of the cylinders with Superior valves (constructed of 316 stainless steel) have produced HCl concentration results that are lower relative to results obtained from Nupro-valved cylinders. Scott Specialty Gases also stated that increasing the sample flow rate (to >1 L/min) through the delivery system reduced the HCl loss within the Superior valves. Their investigation will continue to evaluate and resolve the problem of obtaining a representative HCl gas sample from the cylinders.

The Scott Specialty Gas cylinders used by Entropy throughout the HCl CEM evaluation all have Superior valves. A small amount of corrosion is visible inside each valve and outlet connector. The evidence of oxidation, along with some low cylinder analysis results, indicates that HCl adsorption had occurred within the valves. Although all cylinder gas sampling was conducted at flow rates of 1-3 L/min, the question remains of whether the Superior valves caused a bias in the cylinder gas analysis results, and if so, to what degree. According to gas vendor information, the calibration gas injections to the HCl monitoring equipment should not have been significantly affected by the valve adsorption, because the gas flow rate from the cylinders during those injections was greater than 2 L/min.

An estimate of the rate of HCl decay should not be made with the cylinder gas analysis information presented because of the apparent problem of cylinder valve adsorption and the resulting question of whether a representative sample has been delivered from the cylinder to the impinger train.

3.8 COMPARISON OF ANALYTICAL TECHNIQUES FOR WET-CHEMICAL HCl SAMPLES

To support the evaluation of continuous HCl monitors, relative accuracy testing and HCl calibration gas cylinder analysis were conducted by using a

midget impinger sampling train and equipment similar to EPA Method 6. The techniques chosen for analysis of the impinger samples included a mercuric nitrate titration procedure using EPA Method 325.3 and an IC procedure. The titration procedure was chosen to permit sample analysis in the field to provide rapid feedback on both the operation of the HCl monitors and the representativeness of the impinger train samples. The IC analysis was restricted to the laboratory and provided confirmation of the titration results. The IC analysis was also used to quantify certain samples, such as manifold samples, that were below the quantifiable detection limit of the titration procedure used in the field.

The IC analysis is subject to interference from any ion that has a retention time that is similar to that of the chloride ion. The presence of interfering anions can be determined by experienced analysts through an examination of the strip chart recording and use of standard additions. Interfering anions can usually be separated from the chloride ions by changing the analytical conditions, such as the type and length of anion-exchange column or the eluant strength of the mobile phase. A disadvantage of the IC analysis is the relatively long time required for each analysis because of the slow elution of the sulfate ion.

During the course of the HCl evaluation, more than 100 duct and calibration cylinder gas samples were collected and analyzed by both mercuric nitrate titration in the field and IC analysis in the laboratory. The results of these analyses, expressed in terms of total HCl catch, are presented in Tables 3.9 - 3.12. The samples are grouped according to the days when the titrations were performed. The absolute difference between the two analytical techniques is also shown for each sample. The averages for the analytical results and the average for the absolute differences for each sample group are also presented. The averages of the analytical results were used to calculate the analytical bias and a percent bias relative to the IC average. A percent bias for the average of the absolute differences relative to the IC average was also calculated. The results for these calculations are included in the tables referenced above.

3.9 ESP INLET/OUTLET SAMPLING

At the request of source personnel, HCl continuous monitoring was conducted for a brief period of time at the electrostatic precipitator (ESP) inlet to

TABLE 3.9. COMPARISON OF METHODS FOR ANALYZING DUCT SAMPLES
NOVEMBER 1986 RESULTS (mg HCl)

Sample ID	Ion Chromatography	Mercuric Nitrate Titration	Absolute Difference
		November 12, 1986	
D-4	12.7	11.9	0.8
D-5	8.9	10.8	1.9
D-6	26.6	26.2	0.4
D-7	16.7	17.2	0.5
D-8	29.8	33.9	4.1
Average	18.9	20.0	1.5
Bias of Average Relative to IC		1.1	
Bias as a Percent of IC		5.64%	8.11%
		November 13, 1986	
D-10	11.5	11.3	0.2
D-11	15.6	14.7	0.9
D-12	13.9	13.9	0.0
D-13	17.7	16.9	0.8
D-14	14.7	14.4	0.3
D-15	15.1	14.9	0.2
Average	14.8	14.4	0.4
Bias of Average Relative to IC		-0.4	
Bias as a Percent of IC		-2.82%	2.82%

TABLE 3.10. COMPARISON OF METHODS FOR ANALYZING DUCT SAMPLES
MARCH 1987 RESULTS (mg HCl)

Sample ID	Ion Chromatography	Mercuric Nitrate Titration	Absolute Difference
D-1-A	10.1	9.8	0.3
D-1-B	10.8	10.0	0.8
D-2-A	22.6	19.8	2.8
D-2-B	21.2	22.1	0.9
D-3-A	19.0	19.8	0.8
D-3-B	19.6	20.3	0.7
D-4-A	20.1	20.6	0.5
D-4-B	21.2	21.6	0.4
D-5-A	19.9	20.1	0.2
D-5-B	24.5	24.4	0.0
D-6-A	23.1	24.9	1.8
D-6-B	20.6	21.6	0.9
D-7-A	21.1	20.8	0.3
D-7-B	19.4	19.5	0.1
D-8-A	24.4	24.7	0.3
D-8-B	23.1	23.7	0.5
D-9-A	24.6	25.7	1.1
D-9-B	22.0	22.9	0.9
D-10-A	20.8	22.1	1.3
D-10-B	20.2	25.5	5.3
D-11-A	18.8	19.1	0.3
D-11-B	19.8	18.5	1.3
D-12-A	21.2	22.1	0.9
D-12-B	23.9	25.7	1.8
Average	20.5	21.0	1.0
Bias of Average Relative to IC		0.5	
Bias as a Percent of IC		2.72%	4.96%

Table 3.10 (continued)

Sample ID	Ion Chromatography	Mercuric Nitrate Titration	Absolute Difference
D-13-A	20.2	21.1	0.9
D-13-B	20.2	21.6	1.4
D-14-A	21.8	24.7	2.8
D-14-B	24.2	29.6	5.4
D-15-A	23.7	26.2	2.6
D-15-B	24.1	26.5	2.4
D-16-A	17.9	20.6	2.7
D-16-B	19.1	20.8	1.8
D-17-A	13.2	14.4	1.2
D-17-B	11.3	12.3	1.1
D-18-A	17.9	18.8	0.9
D-18-B	16.2	16.7	0.6
D-19-A	21.1	22.6	1.6
D-19-B	19.9	20.8	0.9
D-20-A	19.6	20.8	1.2
D-20-B	23.8	25.2	1.4
D-21-A	16.9	17.5	0.6
D-22-B	15.6	16.5	0.8
Average	19.2	20.9	1.7
Bias of Average Relative to IC		1.7	
Bias as a Percent of IC		8.71%	8.71%

TABLE 3.11. COMPARISON OF METHODS FOR ANALYZING DUCT SAMPLES
APRIL 1987 RESULTS (mg HCl)

Sample ID	Ion Chromatography	Mercuric Nitrate Titration	Absolute Difference
		April 27, 1987	
D-1	30.0	29.4	0.6
D-2	30.9	30.4	0.5
D-3	30.4	28.9	1.4
D-4	24.3	23.7	0.7
D-5	24.7	24.7	0.1
D-6	21.1	22.1	1.0
D-7	20.7	21.4	0.6
D-8	22.8	22.6	0.1
D-9	23.9	24.2	0.3
D-10	26.8	27.9	1.1
Average	25.6	25.5	0.6
Bias of Average Relative to IC		-0.1	
Bias as a Percent of IC		-0.15%	2.51%
		April 29, 1987	
D-11	20.1	20.6	0.5
D-12	19.0	18.6	0.3
D-13	17.6	18.1	0.5
D-14	20.5	20.6	0.1
D-15	17.0	17.4	0.3
D-16	21.7	21.6	0.1
D-17	18.4	19.4	0.9
D-18	21.1	21.6	0.6
D-19	17.8	18.4	0.5
D-20	18.5	18.9	0.4
Average	19.2	19.5	0.4
Bias of Average Relative to IC		0.3	
Bias as a Percent of IC		1.83%	2.25%

TABLE 3.12. COMPARISON OF METHODS FOR ANALYZING CYLINDER SAMPLES, DECEMBER 1986 and JANUARY 1987 RESULTS (mg HCl)

Sample ID	Ion Chromatography	Mercuric Nitrate Titration	Absolute Difference
		December 3, 1986	
1	96.2	94.8	1.4
2	70.7	70.3	0.4
3	62.5	64.2	1.6
4	21.9	23.1	1.3
5	27.1	29.4	2.3
6	23.0	24.1	1.1
7	18.6	20.3	1.7
8	20.7	22.8	2.2
9	22.2	23.4	1.2
10	74.1	76.6	2.5
11	80.6	83.1	2.5
12	90.9	92.2	1.4
13	6.0	7.2	1.2
14	13.8	15.5	1.8
15	15.0	17.1	2.1
Average	42.9	44.3	1.7
Bias of Average Relative to IC		1.4	
Bias as a Percent of IC		3.24%	4.08%
		January 28, 1987	
7	84.8	83.2	1.6
8	92.3	90.2	2.0
9	77.3	76.6	0.7
13	22.7	23.1	0.5
14	19.5	19.5	0.1
15	29.9	31.6	1.7
16	28.5	33.7	5.2
17	33.8	36.2	2.4
Average	48.6	49.3	1.8
Bias of Average Relative to IC		0.7	
Bias as a Percent of IC		1.38%	3.66%

investigate the capabilities of a dilution probe upstream of particulate control equipment. The TECO dilution probe and sample handling system were moved from the ESP outlet to a sample location upstream of the ESP. The Bodenseewerk monitoring system continued sampling at the ESP outlet location to collect comparative data. Concurrent HCl monitoring at the two locations was performed for three days.

Figure 3-6 graphically presents the ESP inlet and outlet HCl measurements (on a dry basis) provided by the TECO and Bodenseewerk CEMSs. A flue gas water vapor concentration of 13% was assumed in order to correct the wet-basis TECO measurements to a dry basis and thus make a direct comparison between the TECO and Bodenseewerk measurements.

No operational problems were experienced with the TECO dilution probe during this 3-day sampling period. When the probe was removed from the duct, a significant amount of particulate matter had accumulated on the probe. However, the comparison of the two sets of data does not indicate that the buildup of particulate matter on the probe tip adversely affected the TECO measurement data.

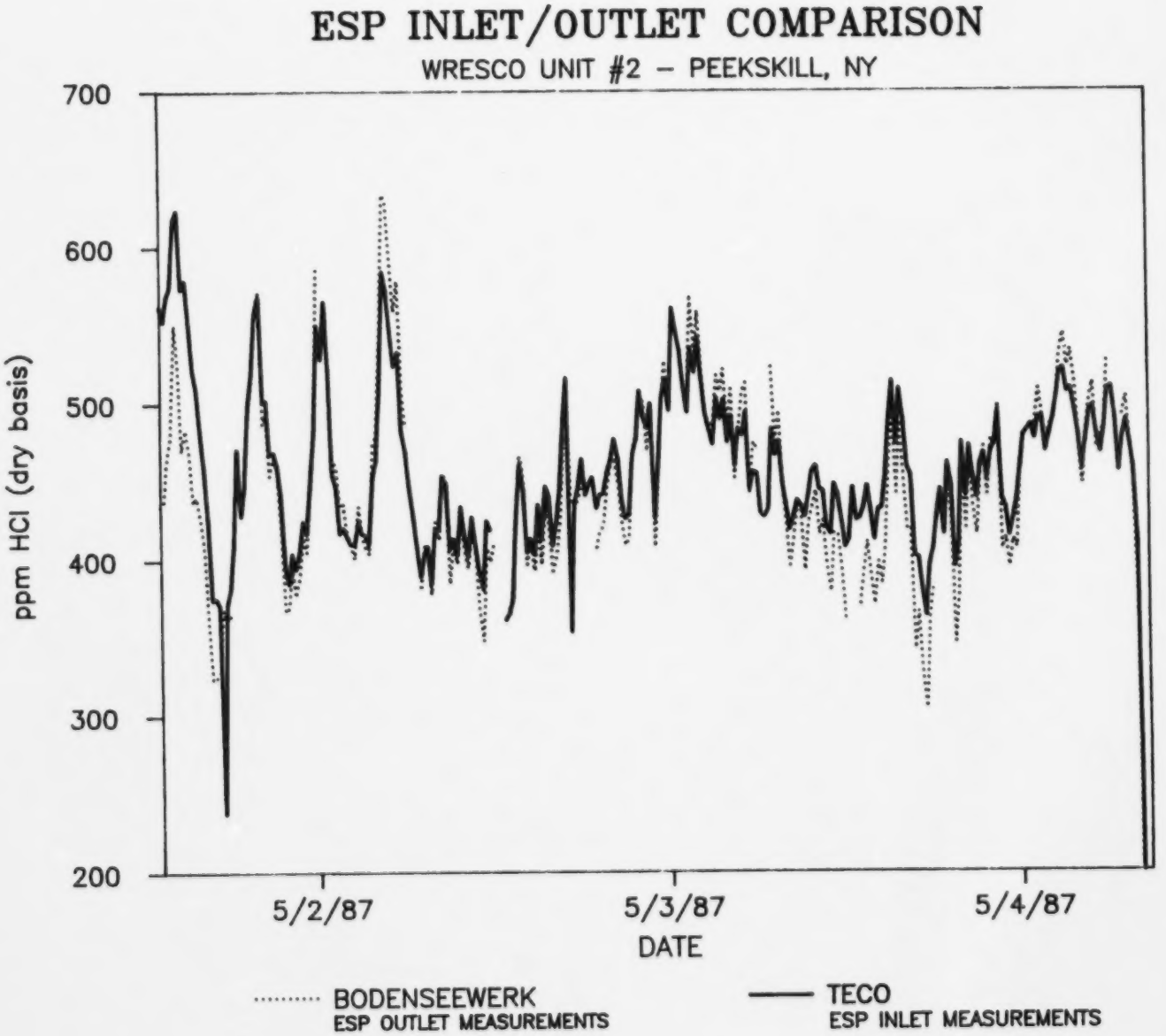

ESP INLET/OUTLET COMPARISON
WRESCO UNIT #2 – PEEKSKILL, NY
700
600
500
400
300
200
ppm HCl (dry basis)
5/2/87
5/3/87
5/4/87
DATE
BODENSEEWERK
ESP OUTLET MEASUREMENTS
TECO
ESP INLET MEASUREMENTS

Figure 3-6.

SECTION 4

EQUIPMENT DESCRIPTIONS AND TEST PROCEDURES

4.1 SOURCE DESCRIPTION

The three units of RESCO's Westchester County plant in Peekskill, New York, are refuse-fired boilers that produce steam necessary to drive turbines for the generation of electricity.

The plant provides a daily disposal of 2250 tons of municipal solid waste (3 units @ 750 tons per day each). As shown in Figure 4-1, incoming trucks dump refuse into an enclosed receiving pit. Overhead cranes transfer the refuse directly from the pit to the feed hopper of each furnace. The refuse is combusted on Von Roll grates within the furnace, where temperatures exceed 2500°F. A waterwall boiler above the combustion bed produces superheated steam; the rated capacity of each unit is 167,700 lb steam per hour. The steam drives a turbine-generator, which produces electricity. The facility sells the electricity to Consolidated Edison Company.

The flue gases exit the boiler and are passed through an economizer, an ESP, and an induced draft (ID) fan before entering the stack where the gases are exhausted to the atmosphere.

Bottom ash and grate siftings are discharged into an ash pit. The ash disposal system separates the metals and aggregate, and then trucks transport the materials from the plant site.

4.2 DESCRIPTION OF SAMPLING LOCATION

All flue gas samples were extracted from the flue gas handling system at the sample port location between the ESP outlet (upstream of the ID fan) and the stack breeching (see Figure 4-2). The sampling location was approximately 35 ft above ground, where the trailer housing the analyzers was located. The figure also shows the placement of each of the sampling probes and their relative position within the duct. Figure 4-3 presents a schematic of the setup of the analyzers and the sampling systems.

The maximum depth the Compur probe extended inside the duct was 1 ft Results of testing previously conducted by Entropy indicated no significant stratification at the sample location. A nonstratified effluent stream, and

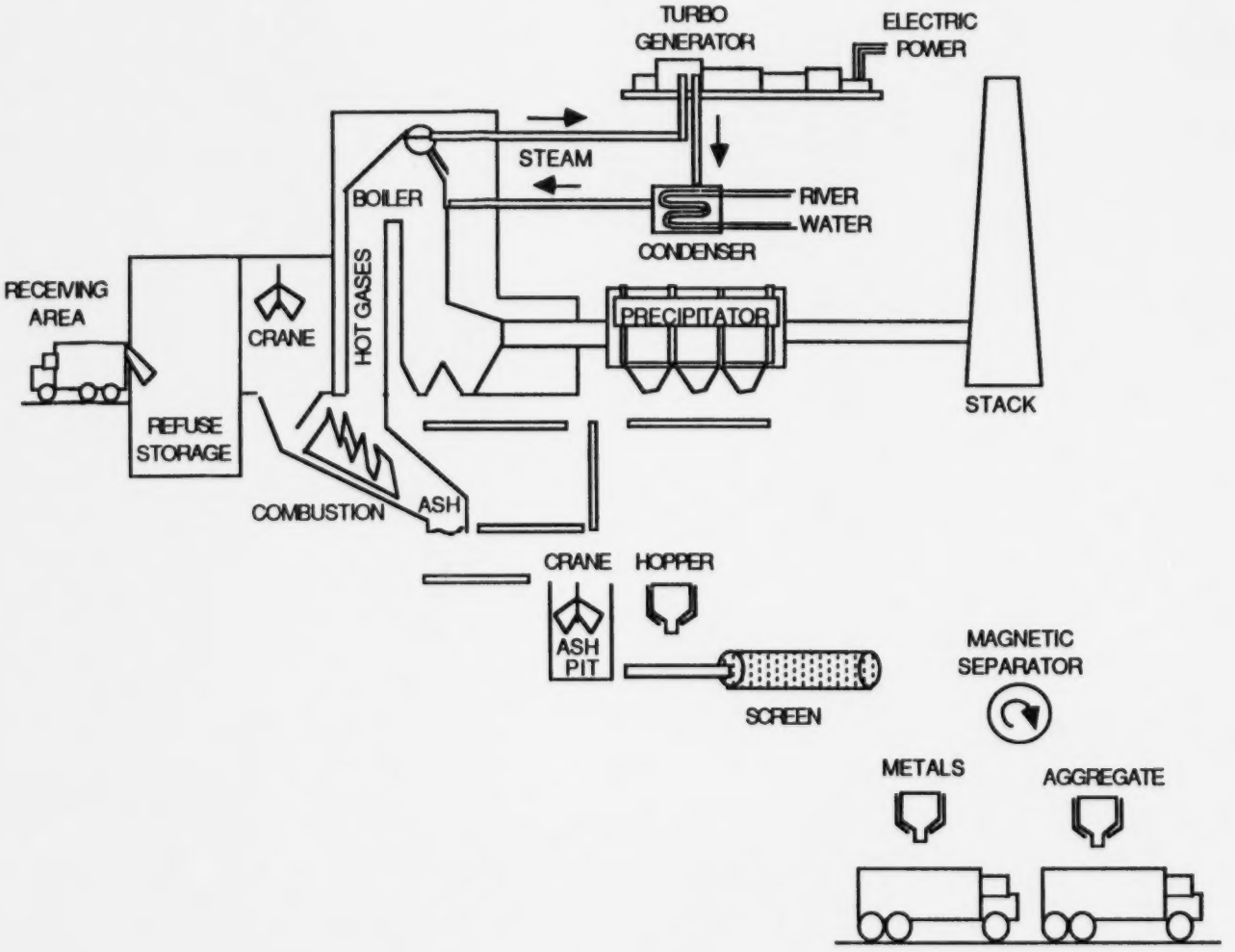


Figure 4-1. Disposal process schematic for RESCO's Westchester County plant.

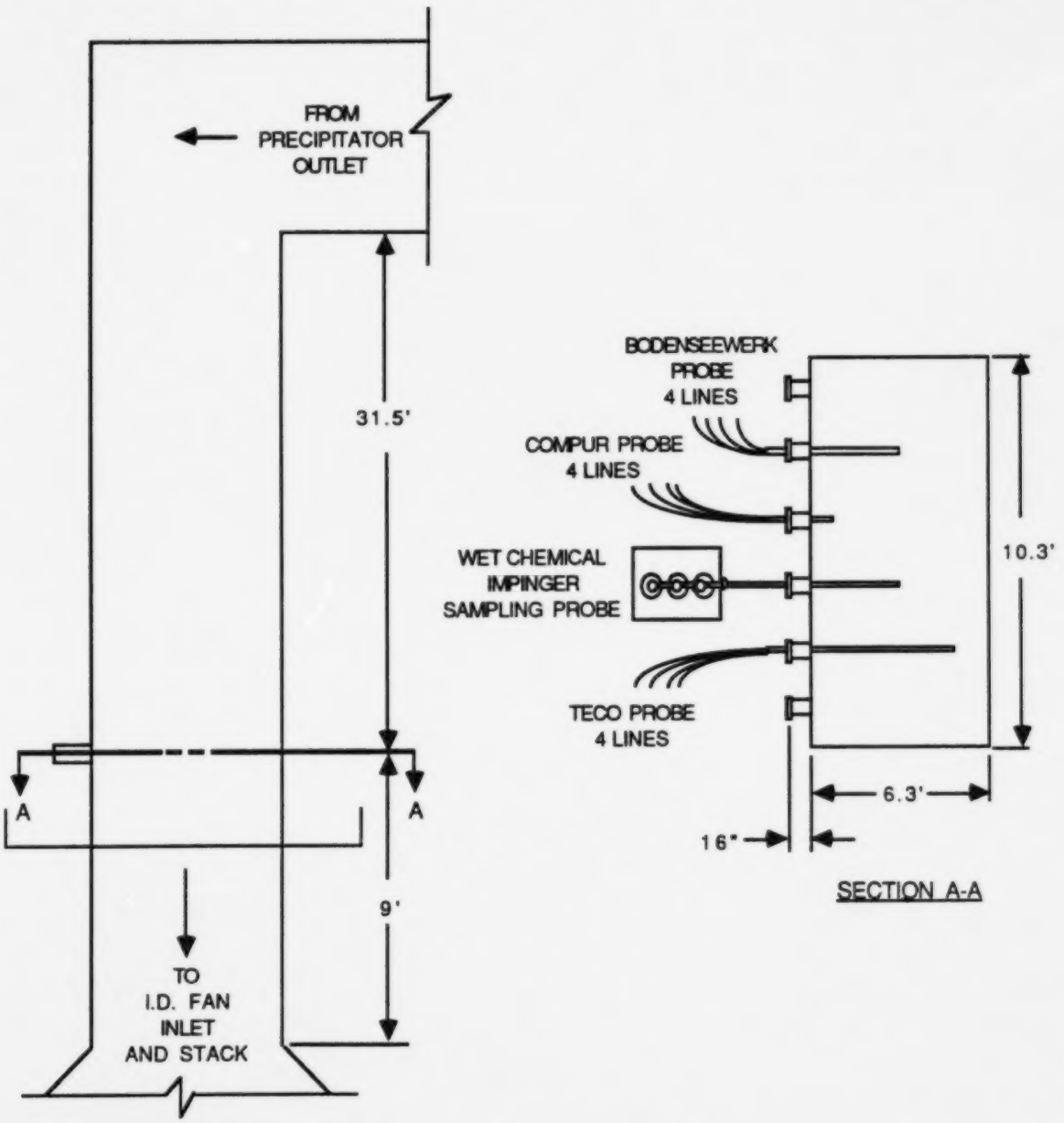


Figure 4-2. Unit 2 ESP outlet sampling location.

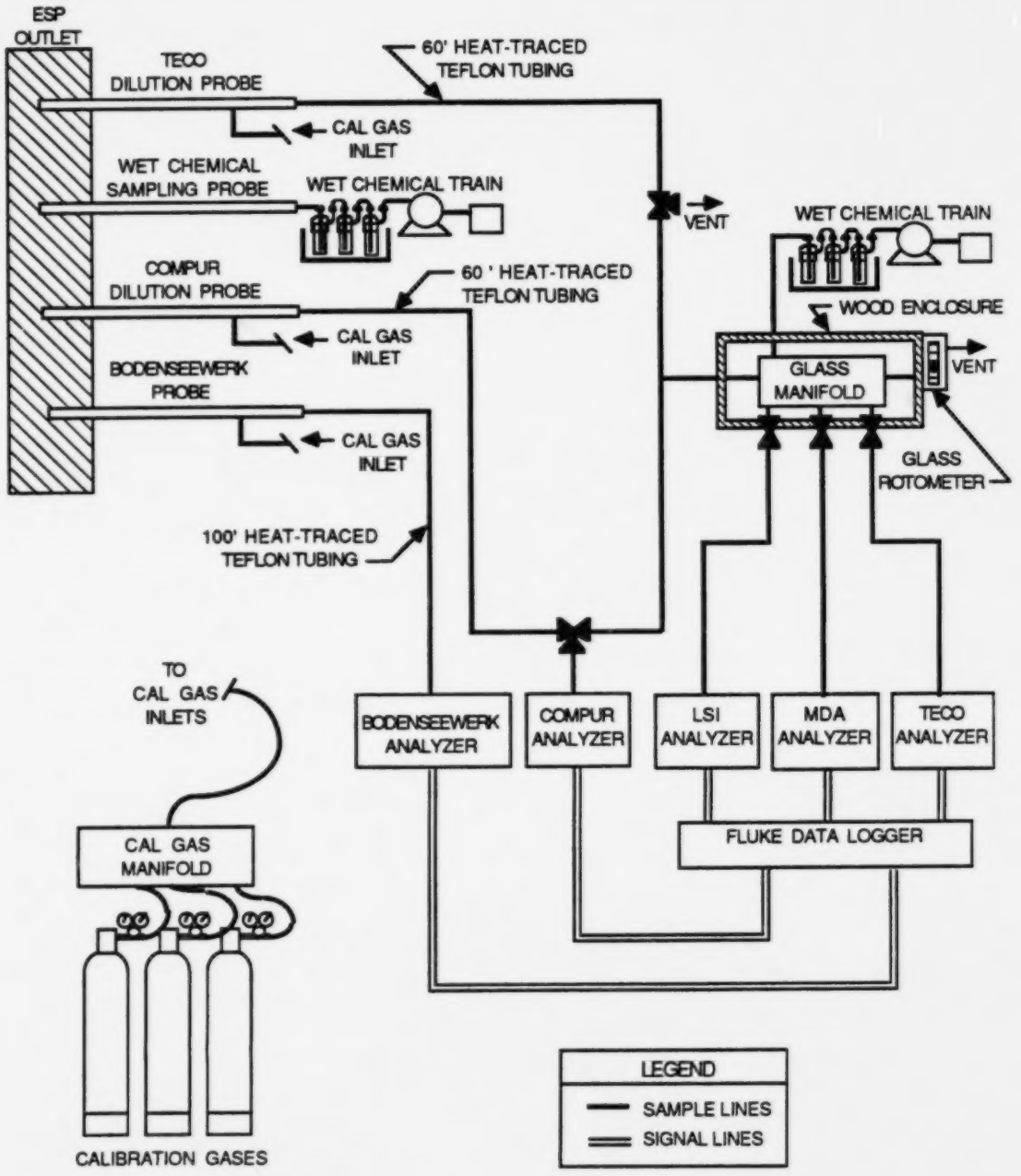


Figure 4-3. HCl monitoring systems schematic.

the ability to adequately seal the probe flange to the port to prevent air in-leakage, eliminated concern about the position of the Compur probe.

Sample lines for each of the sample transport systems were run from the probes down to the EPA trailer on the ground. The lengths of the TECO and Compur sampling system lines were approximately 60 ft. The four lines required for the operation of each dilution probe included (1) a heat-traced Teflon sample transport tube, (2) a Teflon calibration gas transport tube, (3) a dilution air tube, and (4) a probe orifice vacuum line. The Bodenseewerk sampling line was heat-traced and approximately 100 ft long; and the three compressed air tubes for a pneumatic actuator, probe and filter purge, and sample handling system purge were each approximately 60 ft in length.

4.3 HCl CONTINUOUS EMISSION MONITORING SYSTEM DESCRIPTIONS

The following discussions briefly outline the operational principles of the monitoring equipment.

4.3.1 Bodenseewerk Spectran Model 677 IR HCl Monitoring System

The Bodenseewerk 677 HCl analyzer employs the gas filter correlation (GFC) technique with the multiple optical pass cell and sampling system maintained at an elevated temperature of 180°C (356°F). HCl concentrations are recorded on a dry basis within a system operating range of 0-1000 ppm. (The analyzer measurement is made on a wet basis. However, the analyzer was factory calibrated by using HCl calibration gas blended with 15% by volume water vapor. Accordingly, the analyzer concentration readings correspond to a dry measurement. A further detailed explanation provided by Bodenseewerk concerning this issue is included in Appendix E to this report.) The vendor claims the detection limit of this instrument is 1 ppm.

GFC spectroscopy is based upon comparison of the absorption of a selected wavelength within the infrared (IR) absorption spectrum by the measured gas to that of other gases also present in the sample being analyzed. The technique is implemented by using a high concentration sample of the measured gas (i.e., HCl) as a filter for the IR radiation transmitted through the analyzer. The analyzer contains a correlation wheel that consists of two hemispherical cells,

one filled with HCl and the other with N_2. Integral with the correlation wheel is the chopper pattern necessary to produce the high frequency compatible with the IR detector.

Radiation from an IR source is chopped and then passed through the gas filter, alternating between HCl and N_2 as the filter wheel rotates. The radiation then passes through a narrow-bandpass interference filter and enters a multiple optical pass cell, where it is absorbed by the sample gas. The IR radiation then exits the sample cell and is measured by the IR detector.

The HCl gas filter produces a reference beam that cannot be further attenuated by HCl in the sample cell. The N_2 side of the filter wheel is transparent to the IR radiation and therefore produces a measurement beam that can be absorbed by HCl in the cell. The chopped detector signal is modulated by the alteration between the two gas filters with an amplitude related to the concentration of HCl in the sample cell. Other gases do not cause modulation of the detector signal, because they absorb the reference and measurement beams equally. Thus, the HCl GFC system responds specifically to HCl. With the improved rejection of interference afforded by the GFC technique, the sensitivity of the analyzer is increased by using multiple pass optics in the sample cell, which leads to a large path length, and thus an improved sensivity, in a small physical space.

The sample gas is drawn from the effluent via a heated sample pump at a rate of approximately 13 L/min. A coarse, fritted filter is located at the probe tip for filtering particulate matter. The sample gas is heated to approximately 180°C (356°F) and it maintains this temperature throughout the transport system and the sample cell until it is exhausted from the analyzer.

The Model 677 analyzer employs zero air and an internal sealed gas cell for zero and upscale calibration checks. The monitoring system can also accept calibration gases; the gas injection point is located at the probe.

The concentration measurements in units of ppm (dry) are displayed on a front panel meter and are also recorded by a built-in strip chart recorder. A 0-1 V output is provided for an external data-recording device.

4.3.2 Compur Model 4150 ZGSM HCl Analyzer/Model 4330 Dilution System

The Compur 4150 HCl analyzer uses an ion selective electrode (Cl^-) to measure dilute HCl concentrations in a range of 0-150 ppm on a wet basis. Detection limits for this instrument are unknown.

The sample gas is drawn into the analyzer by means of an air aspirator. The sample passes through an atomizer, the measuring cell, and then to the waste reservoir, where the gas is exhausted from the analyzer. A peristaltic pump delivers absorption solution from the storage reservoir to the atomizer, where it is atomized to an aerosol. The HCl in the gas sample passing through the atomizer is scrubbed from the gas by the atomized absorbing solution. A highly enriched solution is produced and passed between two electrodes, a reference and a chloride ion electrode. The concentration-related potential of the electrodes is fed to the microprocessor. The corresponding HCl concentration in units of grams per cubic meter is displayed on a front panel digital display. A 0.2 - 1 V output is provided for a data recorder.

The analyzer performs its own internal calibration automatically at selected time intervals by using a liquid standard. Continuous self-diagnostic routines verify proper operation of the analyzer. The alphanumeric display and built-in printer provide status conditions of the analyzer, alarm functions, and identification of the cause of any malfunctions, as well as continuous updates on the concentration measurements.

Compur developed a dilution probe to be used in conjunction with the Model 4150 analyzer to sample stack emissions. The dilution probe is an extractive sampling device that produces constant sample gas dilutions at selected ratios varying from 10:1 to 100:1. The dilution probe is electrically heated to 200°C (392°F) and is constructed of stainless steel and molybdenum.

An air jet pump within the probe acts as an in-stack dilution device by aspirating the flue gas sample through an orifice and diluting the gas sample with dry regulating air. By reducing the pressure downstream of the orifice with the aspirator air, a constant flow of flue gas sample is drawn through the orifice and mixed with the aspirator air. The orifice operates within the critical region, strongly reducing the influence of pressure fluctuations at the sampling point, which tend to affect the flow of sample gas and thereby change the dilution rate.

Calibration of the system is performed by injecting calibration gas through a transport tube to the probe at a point upstream of the critical orifice.

Thus, the calibration gas is conditioned in the same manner as the flue gas sample (i.e., filtered, diluted, and transported).

The Model 4150 analyzer continuously monitors all Model 4330 dilution system parameters, such as probe temperature, pressures, and flow rates. The analyzer's microprocessor calculates the actual HCl concentrations present in the effluent by correcting the analyzer measurements for the dilution ratio selected by the operator.

4.3.3 Thermo Electron Model 15 HCl Analyzer/Model 200 Dilution System

The Thermo Electron (TECO) Model 15 GFC HCl analyzer is an analytical instrument for continuous, real-time measurement of HCl on a wet basis. For a discussion of GFC spectrosopy and IR radiation, see Section 4.4.1.

Because IR absorption is a nonlinear measurement technique, the instrument electronics transfer the basic analyzer signal into a linear output. The exact calibration curve is stored in the computer's memory and is used to linearize the instrument output over all the ranges. The microcomputer is used to process signals from both a pressure and temperature transducer to make corrections to the instrument output, resulting in HCl concentration measurements that are unaffected by changes in the temperature or pressure of the sample gas.

The analyzer has 10 selectable operating ranges from 0-5 ppm up to 0-5000 ppm HCl. The analyzer was operated on the 0-100 ppm full-scale range. The vendor claims that the detection limit for this instrument is 0.1 ppm.

The Model 200 dilution system comprises the following components:

- in-situ dilution probe with sample orifice,
- transport tubing, and
- M200 stack probe control unit.

The dilution probe is designed to extract a small amount of sample continuously through a fine filter. The sample flow rate is precisely controlled to within 2% by a glass critical orifice of low coefficient of expansion. By reducing the pressure after the fine filter with a precision aspirator to create a vacuum of 0.46 bar in the volume downstream of the critical orifice, a constant flow of flue gas sample is drawn through the orifice, thoroughly mixed with the aspirator air, and then transported through the sample line to the appropriate analyzer.

The sampling system is designed to permit stepwise dilution ratios of 12:1 to 350:1 within the probe by a single selected orifice.

All calibration is performed by introducing calibration gas through the calibration line to a point within the probe upstream of the first fine filter in the probe dilution orifice. In this way, the calibration gas follows all of the sample conditioning steps taken by the flue gas sample.

The lines transporting flue gas sample and calibration gas are Teflon, and the dilution air and vacuum lines are polyethylene.

The dilution air and calibration gas flow controls are contained within the M200 control unit.

4.3.4 Lear Siegler, Inc. LSI/CEA Instruments Model TGM-555 HCl Analyzer

The LSI/CEA TGM-555 analyzer is an automated wet-chemical colorimetric analyzer. The analyzer measures the HCl concentration in the gas sample on a dry basis by monitoring the amount of color change produced in the analyzer's reagent system. The instrument operates within a range of 0-50 ppm, and the vendor claims the detection limit for this analyzer is 0.5 ppm. The sample gas is continuously drawn into the analyzer via an internal vacuum pump, and it passes through a vertical glass/liquid contact absorber coil. The absorbing solution is drawn from its reservoir by a peristaltic pump and is transported concurrently downward with the gas sample through the absorber coil to absorb the HCl within the gas. A two-stage liquid/air separator removes the scrubbed sample gas, which is exhausted. The chemical reaction of the HCl present in the gas sample with the absorbing solution produces a color change in the absorbing solution. The reacted reagent continues along the transport system.

Unreacted reagent is pumped first through the reference cell of the dual-beam colorimeter. The reacted (or colored) solution flows through the sample cell. The colorimeter measures the light absorption of the reagent before and after the reaction with the HCl gas. Transmission of light through the flow cells is measured by a matched set of photodetectors at a particular wavelength. The intensity of the color is directly proportional to the concentration of the HCl.

The electrical signal generated in the colorimeter is amplified and fed to a front panel digital display, where it is read as a percentage of full scale (50 ppm, dry). A 0-1 V output is provided for a data recorder.

The 3.5-L reagent reservoirs that are stored outside the unit hold a nominal 6-day supply.

4.3.5 MDA Model 7100 HCl Gas Analyzer

The MDA 7100 analyzer's detection technique is colorimetry-based and uses dry reaction substrates formulated for a specific gas (Chemcassette detection media).

A sample is drawn from the stack and delivered to a glass manifold via either the TECO or Compur dilution probe. A pump within the Model 7100 analyzer draws the sample from the glass manifold through the Chemcassette in the analyzer. The sampled gas reacts with the chemicals on the Chemcassette tape and forms a stain that is simultaneously read by the electro-optical sensing system. The analog signal produced by the optics system is converted to a digital signal and compared to values stored in the microprocessor memory, and a concentration value is determined. The higher the concentration of the gas, the darker the stain that will appear. The concentration value is shown on the front panel digital display and also can be printed on tape by the built-in printer.

For optimum accuracy and performance, MDA recommends that calibration be checked whenever the Chemcassette detection tape is replaced. The calibration check is accomplished either electronically with a calibration card supplied with the instrument or dynamically with a calibration gas. The calibration card, or "stain card," is a durable polyvinyl chloride card supplied by MDA with simulated zero and span stains, which are used to adjust the calibration factor (Q) of the analyzer. The values on the calibration card are directly traceable to the original dynamic gas calibration performed at the time of manufacture. The Q factor is a multiplication value and is used to calibrate the electro-optical system. The Q factor is self-adjusting each time the "stain card" calibration is performed, and it serves as a basis for readjusting the zero and span of the instrument.

Periodically the sample line filter must be replaced and the optics block cleaned. Otherwise, the only regular maintenance required is Chemcassette replacement, which is usually necessary at approximately 8-9 day intervals.

The Model 7100 analyzer is designed to provide a record of ambient air conditions. The analyzer features dual-level concentration alarms, which may be programmed to alarm at any two concentration levels within the measuring

range of the instrument. When concentrations exceed programmed alarm levels, the date, time, and concentrations are printed. The analyzer may be used to document concentration on a minute-by-minute basis and to document accumulated 8-h time-weighted averages. The analyzer also features an internal diagnostics system, which continually monitors and verifies proper operation of the optics and tape transport systems.

The instrument operating range is 0-100 ppm HCl (wet basis). The vendor claims the lower detectable limit is 0.2 ppm. The gas sample flow rate required for proper measurement is 800 cm^3/min. A 4-20 mA output is provided for hookup to an external data-recording device.

4.4 SAMPLING AND ANALYTICAL PROCEDURES FOR HYDROGEN CHLORIDE

The procedure for wet-chemical impinger sampling of HCl from incinerator emissions, from the common analyzer manifold, and from calibration gas cylinders involved absorbing the HCl in a NaOH solution. The samples collected at Peekskill were first analyzed in the field by mercuric nitrate titrations, and they were later returned to Entropy's laboratory for IC analysis.

The purpose of wet-chemical impinger sampling was to collect HCl concentration measurements to compare to the HCl monitoring measurements so that relative accuracy could be determined. Flue gas sampling was conducted simultaneously at two locations to facilitate quantification of HCl sample line losses. The two locations were the duct and the CEMs' common manifold. The manifold distributed diluted flue gas sample to the CEMs that was delivered from one of the two dilution probes located at the duct. For the two relative accuracy tests conducted in March 1987, duplicate wet-chemical impinger samples were collected at both the duct and the diluted sample manifold locations to minimize the impact of imprecision in the sampling method. Very good agreement was observed between the results of the duplicate samples. Accordingly, only single samples were collected for the April 1987 relative accuracy tests.

The HCl within the flue gas samples was collected with a sampling train similar to a Method 6 train. The absorbing reagent, 15 mL of 0.1 N NaOH, was added to each of the first two impingers. The reagent was used in the manifold impinger trains at 0.001 N NaOH because of the lower HCl content after dilution by the dilution probe. The third impinger (a Mae West design) was filled with calcium sulfate (Drierite) to protect the Singer dry gas meter from moisture.

The desired sampling rate during the relative accuracy testing was 2 L/min with a sampling time of 20 min.

The sampling systems used for the duct sample consisted of all-glass components that contacted the stack gases. A glass-lined probe and glass components were used to convey the stack gas to the duct impinger train. A three-way glass valve was mounted in-line directly upstream of the first impinger.

An important modification for the duct sampling system was to maintain the gas sample temperature above the water dew point until the sample reached the first impinger. This was accomplished by wrapping a heating element around the glass components between the probe and the first impinger.

The sampling system used to collect diluted flue gas samples from the manifold consisted of Teflon and glass components. However, 316 stainless-steel valves were mounted on the manifold to control sample flow, and the gas samples passed through these valves before entering the impinger train.

Purging the sampling system upstream of the impingers with sample gas for 10 min prior to collecting gas cylinder samples was performed. Without the purging, the first sample result was usually lower than the subsequent sample runs. This indicated that the sampling system requires some HCl preconditioning.

The sample recovery involved quantitatively collecting the first impinger's contents separately from the contents of the second impinger. This method was used to permit a check on the sampling train collection efficiency. The collection efficiency of the sampling train for stack samples and gas cylinder samples was good; typically, 99% of the HCl was collected in the first impinger. Deionized (DI) water was used to rinse the sampling train components. The total volume for each sample and rinse was kept to less than 100 mL. All of the samples collected were stored in glass containers.

For analysis, the samples were quantitatively transferred to 100-mL volumetric flasks and volumed to 100 mL with DI water. The mercuric nitrate titrations of the duct flue gas and calibration gas samples in the field were performed according to EPA Method 325.3 (Methods for Chemical Analysis of Water and Waste, EPA 600/4-79-020). The mercuric nitrate titration uses a bromophenol blue - diphenylcarbazone mixed indicator to signal the end point of the titration. Several factors can influence the results of this titration procedure. The presence of SO_3^{2-} in the impinger samples has been shown to cause a significant positive bias in the results. However, by using a 1 mL

portion of 30% H_2O_2, the SO_3^{2-} can be converted to SO_4^{2-} and thus the bias is eliminated. The H_2O_2 treatment procedure was used on all duct samples. A 5-mL aliquot of each sample was pretreated with 30% hydrogen peroxide to eliminate SO_3^{2-} interference.

Heavy metal cations have also been shown to interfere by affecting the color of the end point or preventing the end point formation entirely. By passing an aliquot of the sample through a cation-exchange column, the interfering cations can be removed. A few samples were selected for pretreatment with the cation-exchange resin. The cation-exchange procedure was found unnecessary for duct samples collected from the source where the evaluation program was being conducted. Also, an interfering agent affecting the end point formation in the HCl calibration gas cylinder samples was evidenced by the appearance of a brown color before the final end point was achieved. This problem was eliminated by diluting the sample aliquot by an equal volume of DI water during preparation of the sample for titration.

IC analysis was performed on all collected samples in Entropy's laboratory in conjunction with a Perkin-Elmer high-performance liquid chromatograph (HPLC). The IC analysis uses an anion-exchange column to separate the chloride ion, dissociated in the impinger matrix during sampling, from the other ions present. An ultraviolet-absorbing solution, called a mobile phase or eluant, is used to carry the ions through the anion-exchange column to the analytical detector. The separated chloride ions pass through an ultraviolet detector, resulting in a decrease in the background absorbance of the mobile phase. The detector is connected to a strip chart recorder and an electronic integrator. As the chloride ion passes through the detector, the electronic output from the detector results in a "peak" on the strip chart. The chloride ion is identified basis of the elapsed time, commonly called retention time, between injection of the sample into the chromatograph and the appearance of a peak on the strip chart. The area under the chloride peak is used to quantify the amount of chloride in the sample. Standard solutions of chloride ions are used to calibrate the IC instrument.

The analysis was performed by nonsuppressed IC on a low-capacity resin-based ion exchange column (Hamilton PRP-X100) with a 1.0 mM phthalate mobile phase in which the pH was adjusted to 4.5 with a saturated sodium borate solution. The 40-mL aliquots of each sample used for the IC analysis did not require any pretreatment other than a 20-fold dilution with DI water.

The quantifiable detection limit for this sampling and analysis procedure was 4 ppm HCl for the IC analysis and 20 ppm HCl for the mercuric nitrate titration with a 5-mL aliquot. The manifold samples were analyzed by IC only, because the collected quantity of HCl (5-10 ppm) was below the quantifiable detection limit of the titration.

REFERENCES

U.S. Environmental Protection Agency. Code of Federal Regulations. 40 CFR 264.

Entropy Environmentalists, Inc. (Initial findings of the laboratory and field evaluations, status report). January 1987.

Federal Register 48(102):23608 (May 25, 1983).

U.S. Environmental Protection Agency. 1979. Methods for Chemical Analysis of Water and Waste. EPA 600/4-79-020. Research Triangle Park, NC: U.S. Environmental Protection Agency.

APPENDIX A.

GRAPHIC PRESENTATION OF CEM
MEASUREMENT DATA

- Individual Graphs During
  Relative Accuracy Periods

  - LSI
  - Bodenseewerk
  - TECO
  - MDA
  - Compur

- Individual Graphs During Relative Accuracy Periods

  - LEAR SIEGLER, INC.

Figure A-1 **RELATIVE ACCURACY TEST - 3/19/87**

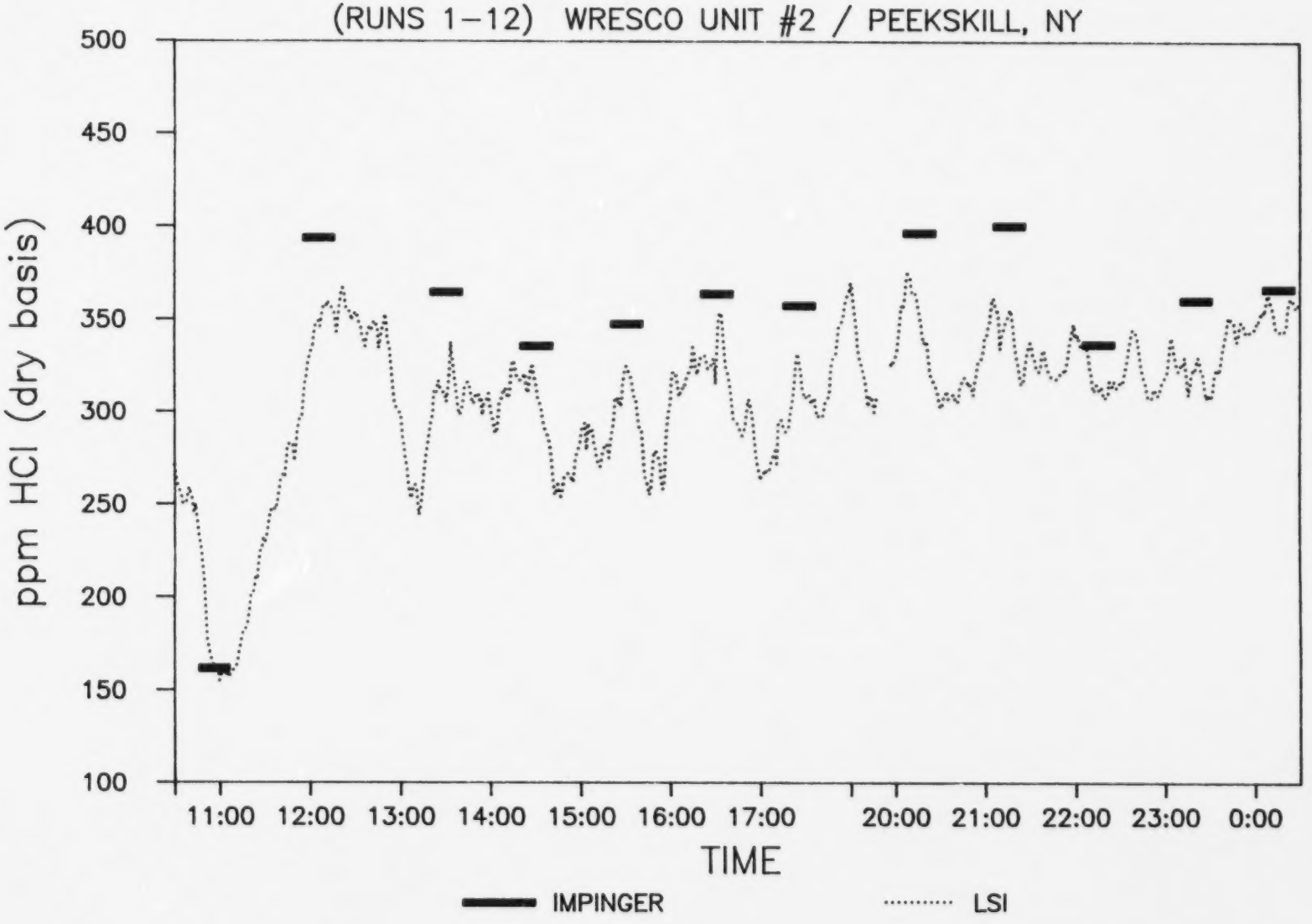


Figure A-2 **RELATIVE ACCURACY TEST - 3/20/87**

(RUNS 13-21) WRESCO UNIT #2 / PEEKSKILL, NY

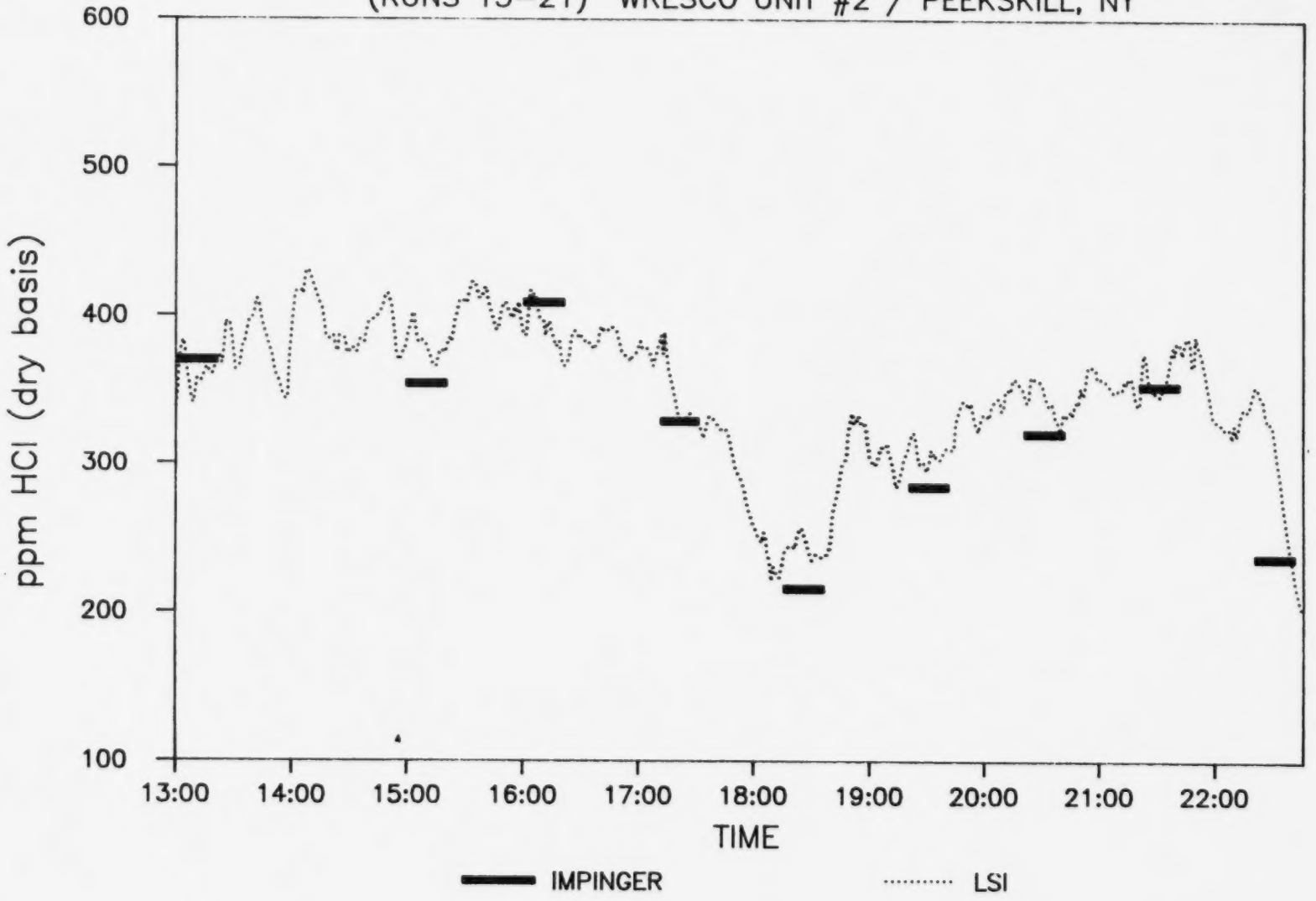


Figure A-3 **RELATIVE ACCURACY TEST - 4/27/87**

(RUNS 1-10) WRESCO UNIT #2 / PEEKSKILL, NY

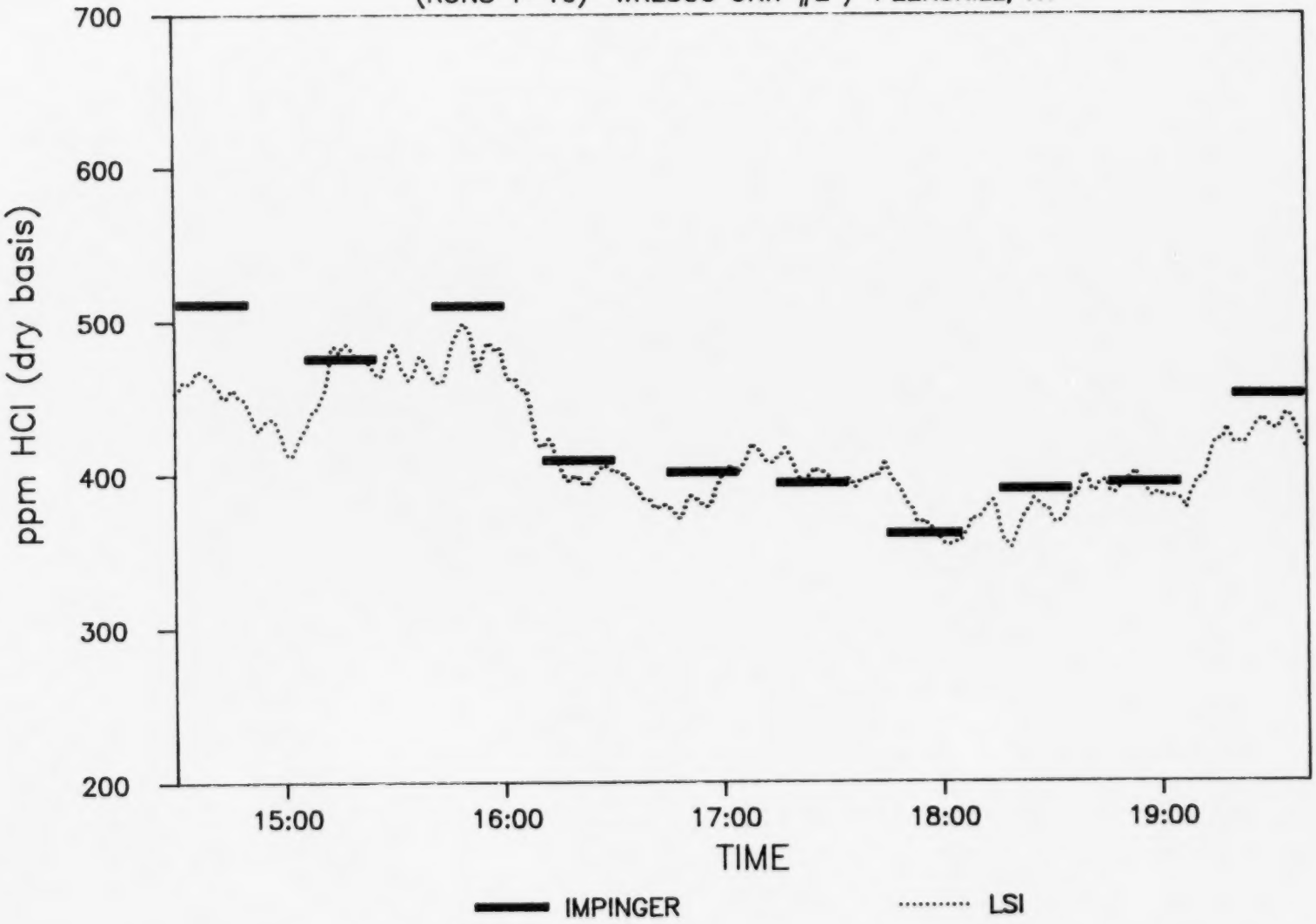
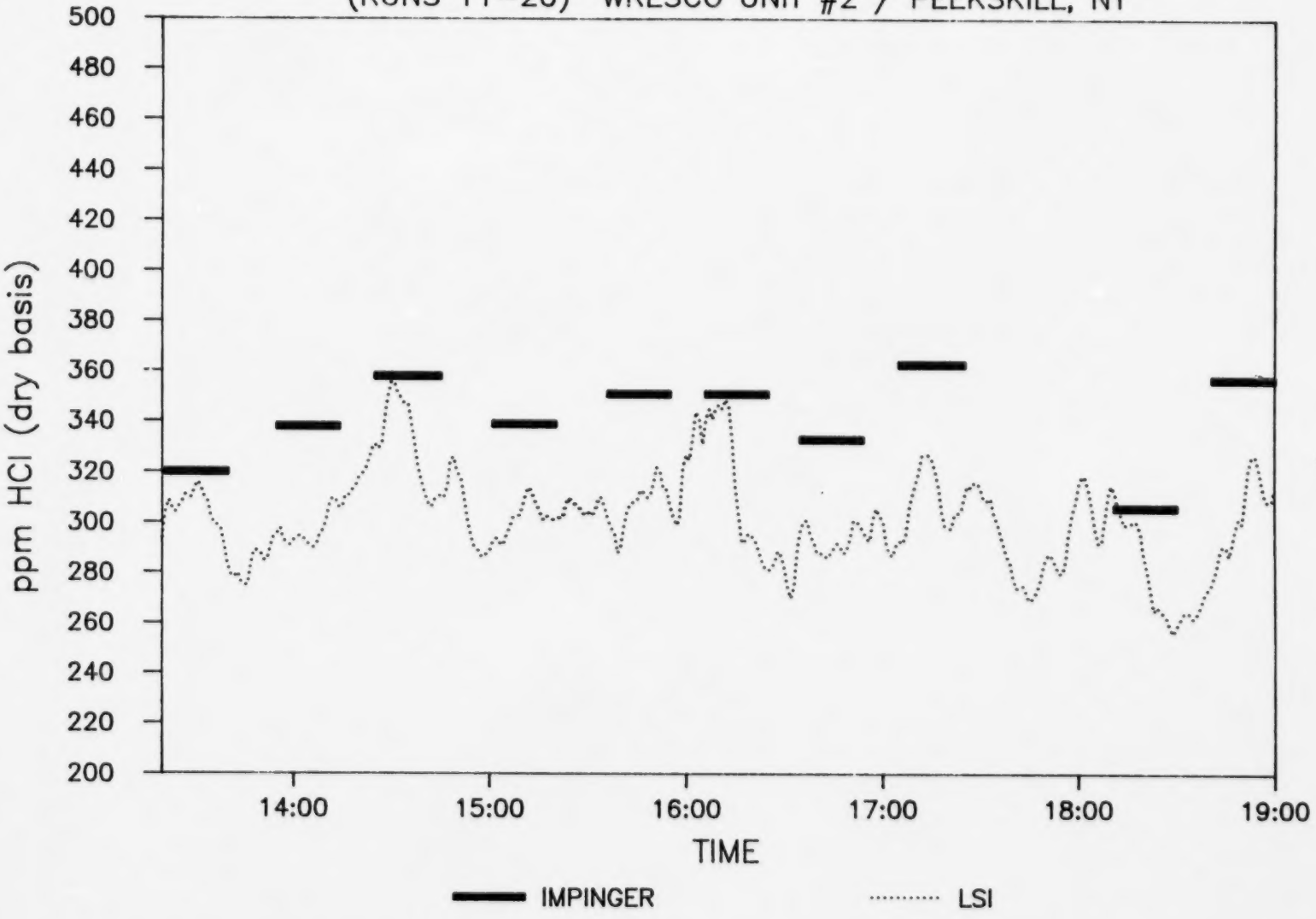


Figure A-4 **RELATIVE ACCURACY TEST - 4/29/87**

(RUNS 11-20) WRESCO UNIT #2 / PEEKSKILL, NY



- Individual Graphs During Relative Accuracy Periods

  - BODENSEEWERK

Figure A-5 **RELATIVE ACCURACY TEST - 3/19/87**

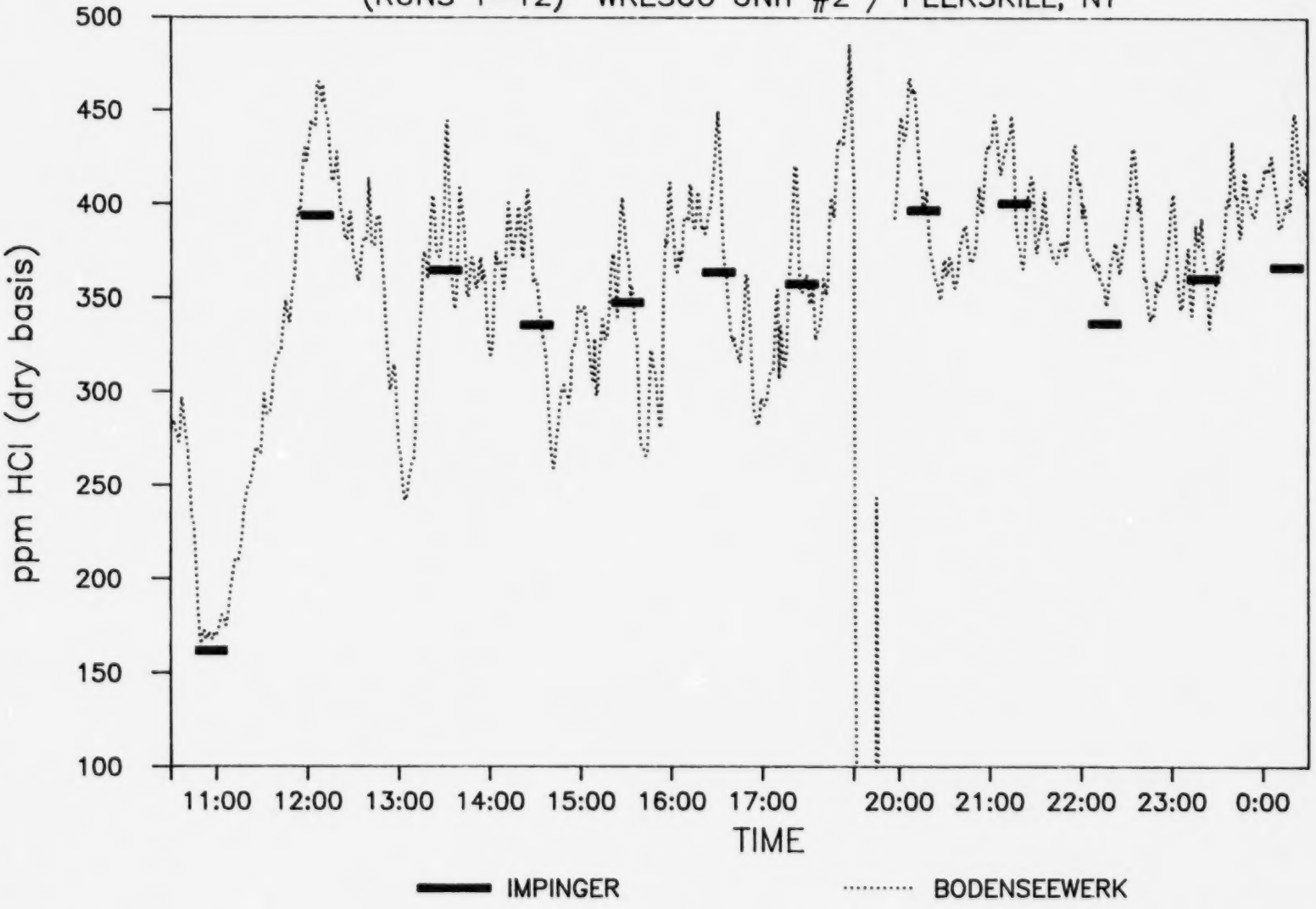


Figure A-6 **RELATIVE ACCURACY TEST - 3/20/87**

(RUNS 13-21) WRESCO UNIT #2 / PEEKSKILL, NY

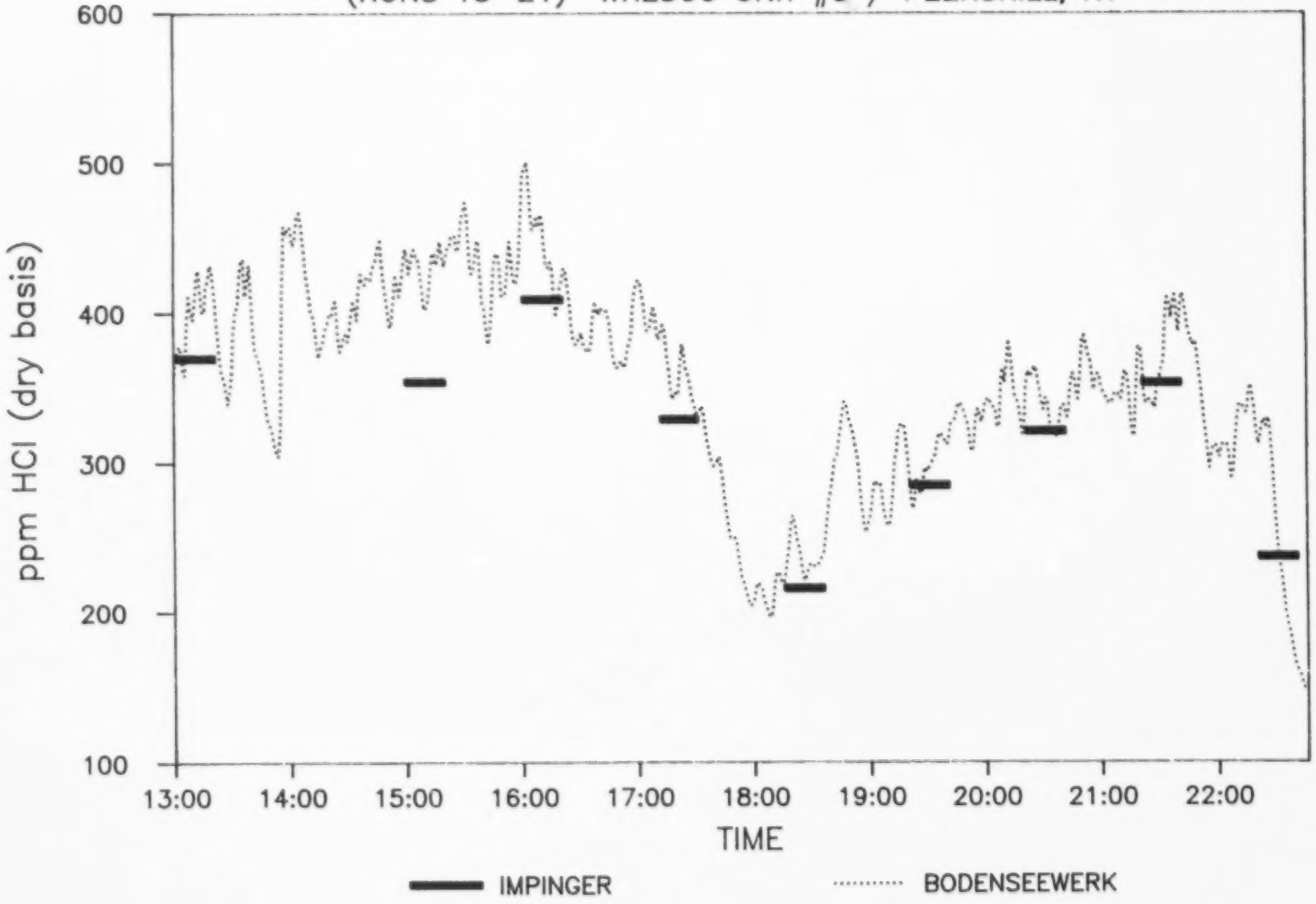


Figure A-7 **RELATIVE ACCURACY TEST - 4/27/87**

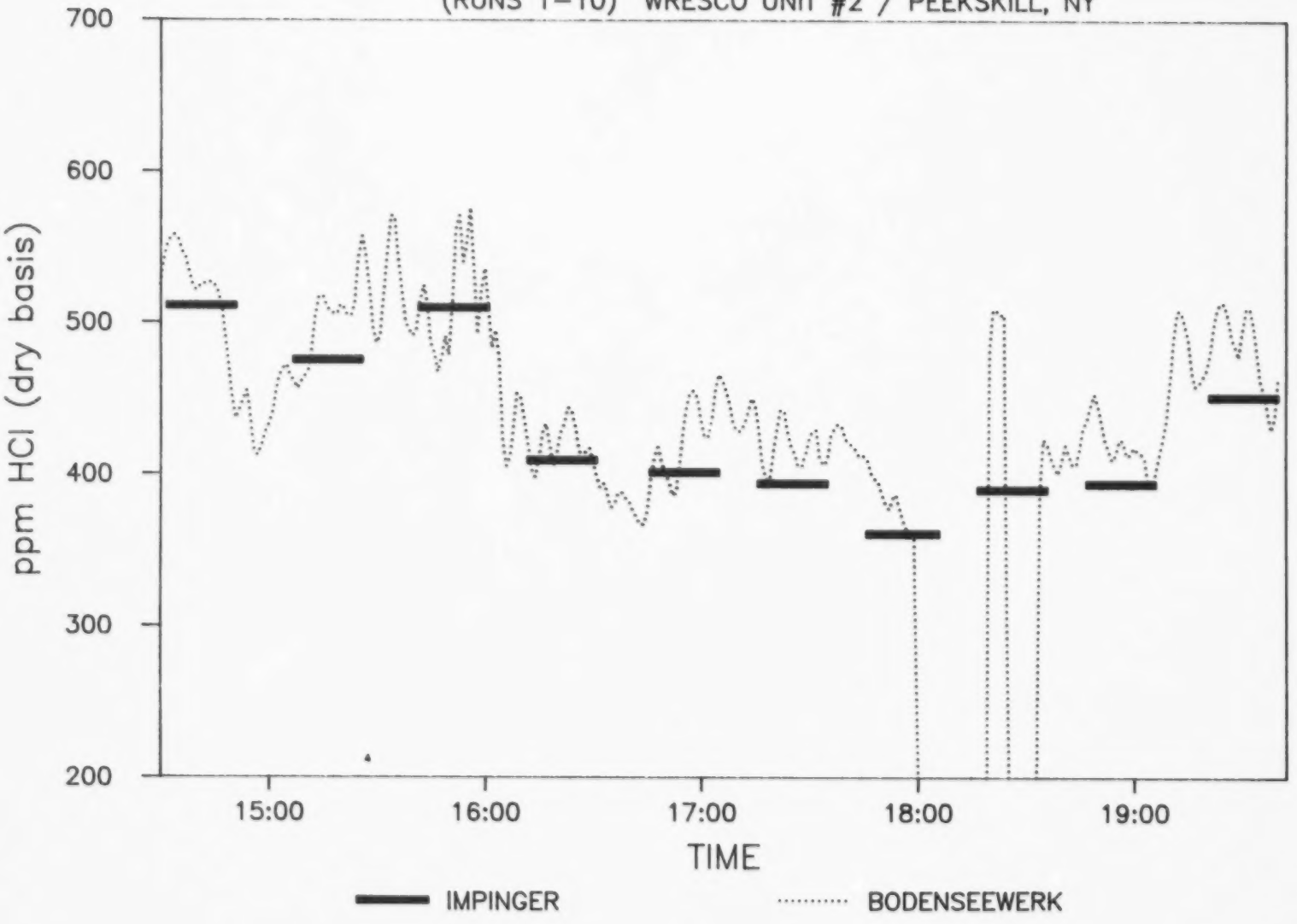
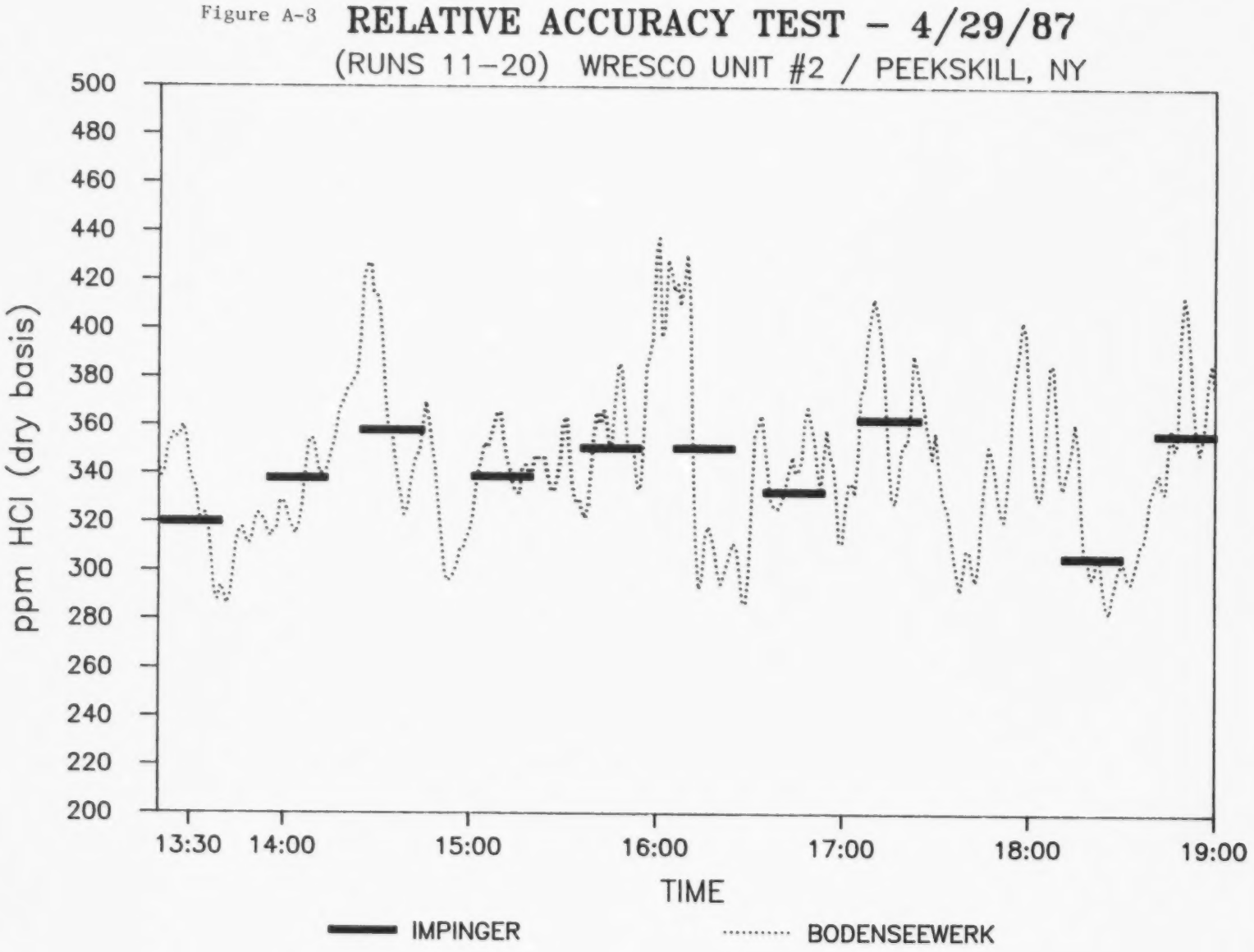


Figure A-8


RELATIVE ACCURACY TEST - 4/29/87
(RUNS 11-20) WRESCO UNIT #2 / PEEKSKILL, NY
ppm HCl (dry basis)
500
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
13:30
14:00
15:00
16:00
17:00
18:00
19:00
TIME
IMPINGER
BODENSEEWERK

- Individual Graphs During Relative Accuracy Periods

  - TECO

Figure A-9 **RELATIVE ACCURACY TEST - 3/19/87**

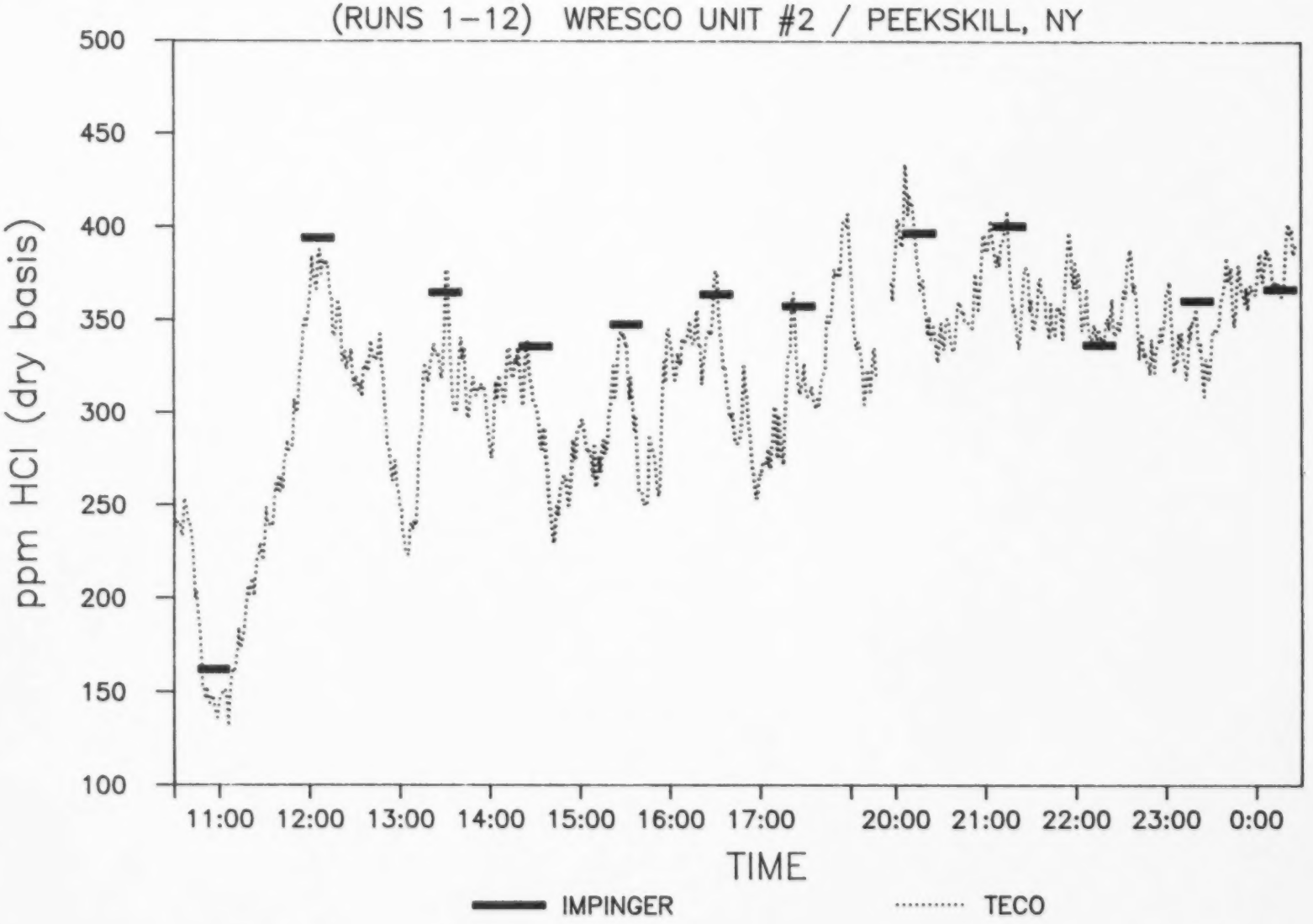


Figure A-10 **RELATIVE ACCURACY TEST – 3/20/87**

(RUNS 13–21) WRESCO UNIT #2 / PEEKSKILL, NY

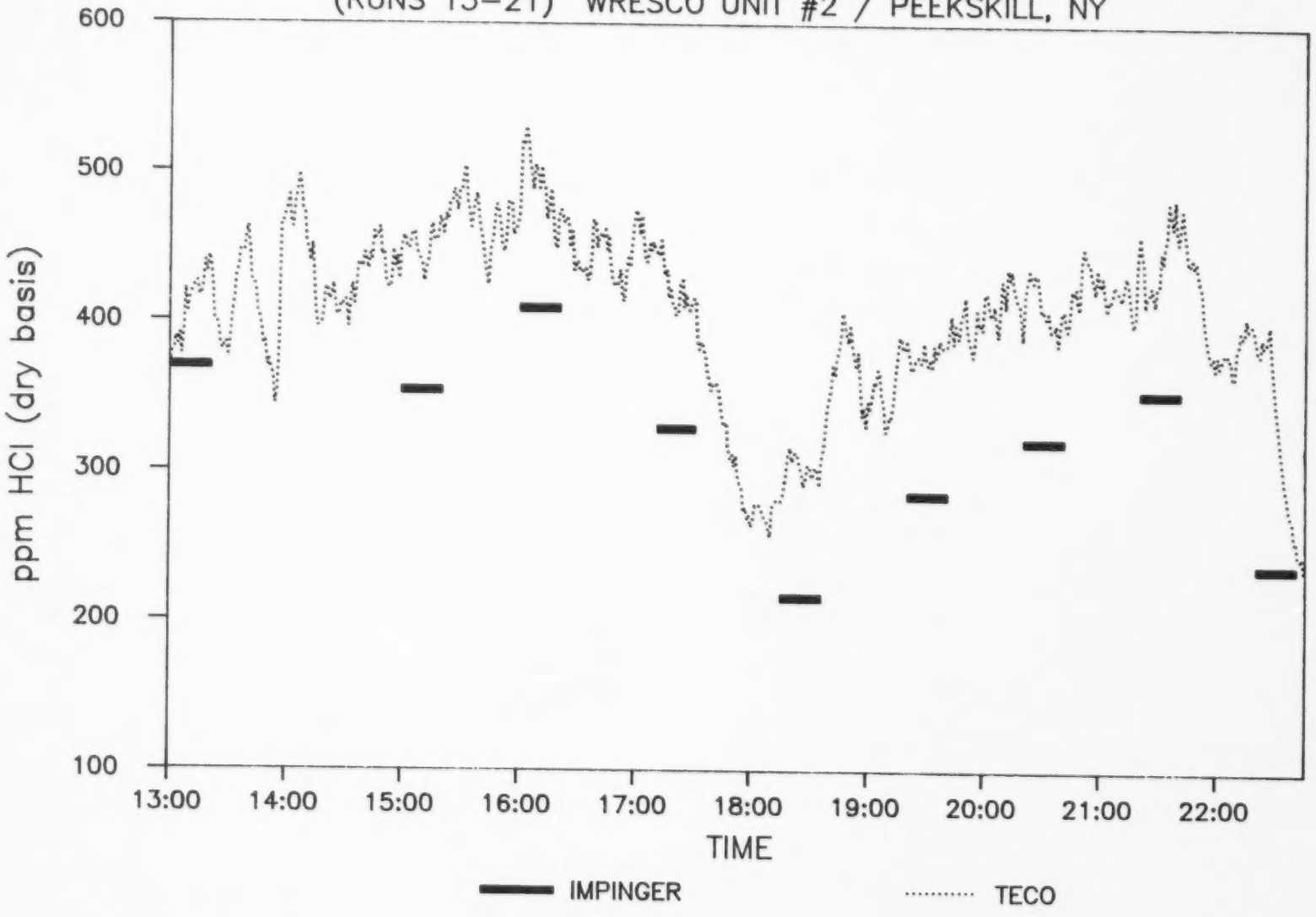


Figure A-11 **RELATIVE ACCURACY TEST - 4/27/87**

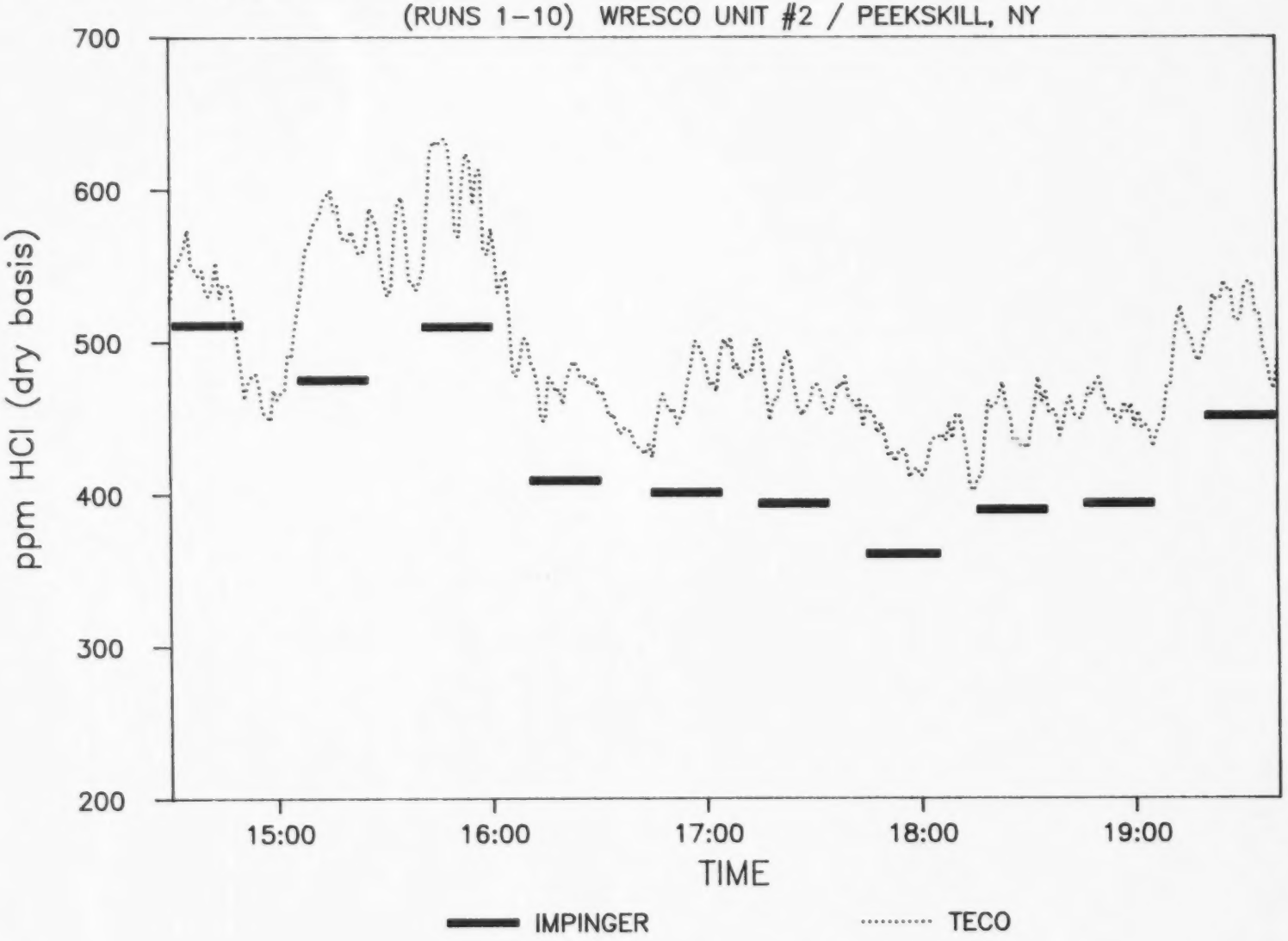
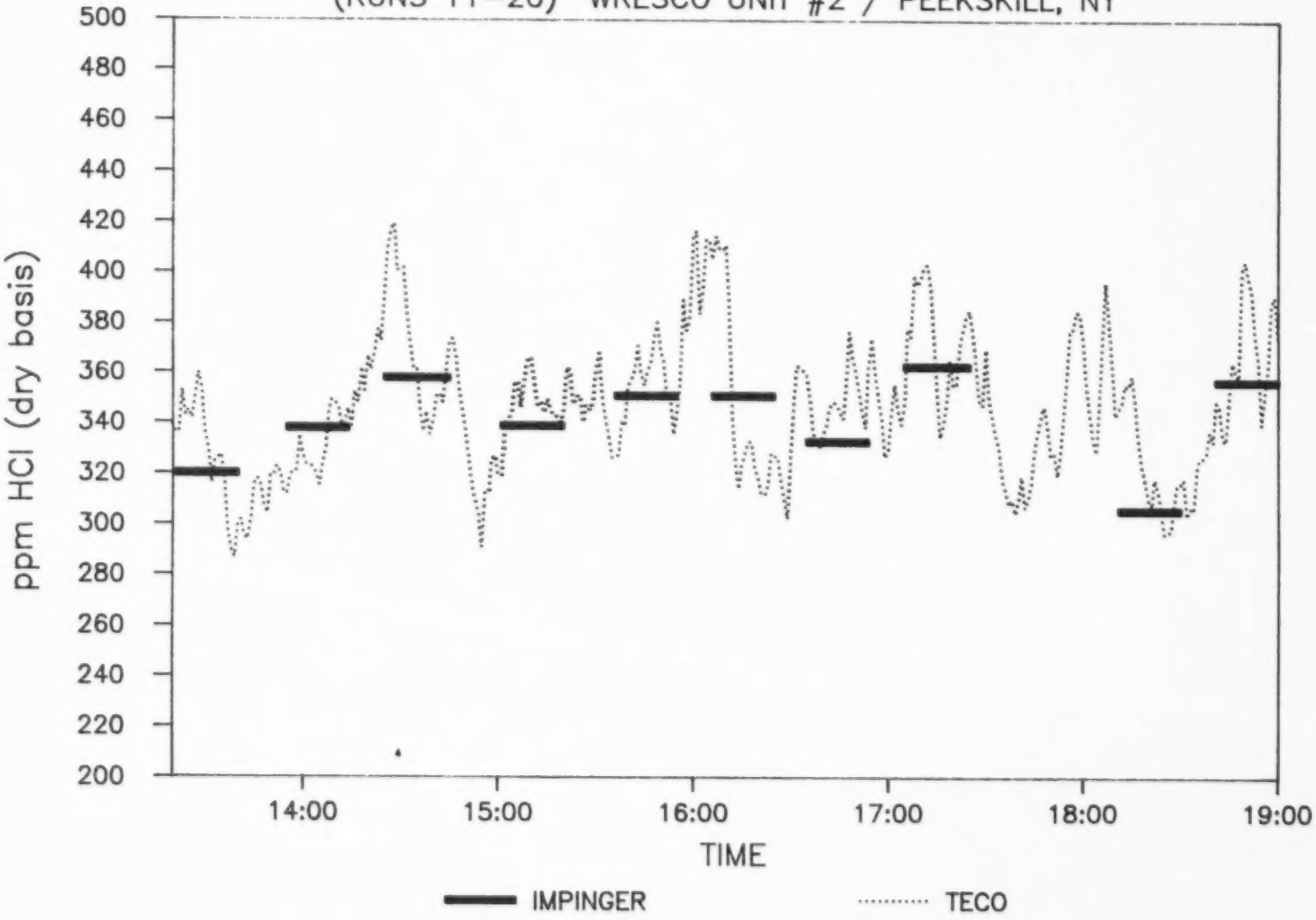


Figure A-12 **RELATIVE ACCURACY TEST - 4/29/87**

(RUNS 11-20) WRESCO UNIT #2 / PEEKSKILL, NY



- Individual Graphs During Relative Accuracy Periods

  - MDA

Figure A-13 **RELATIVE ACCURACY TEST - 3/19/87**

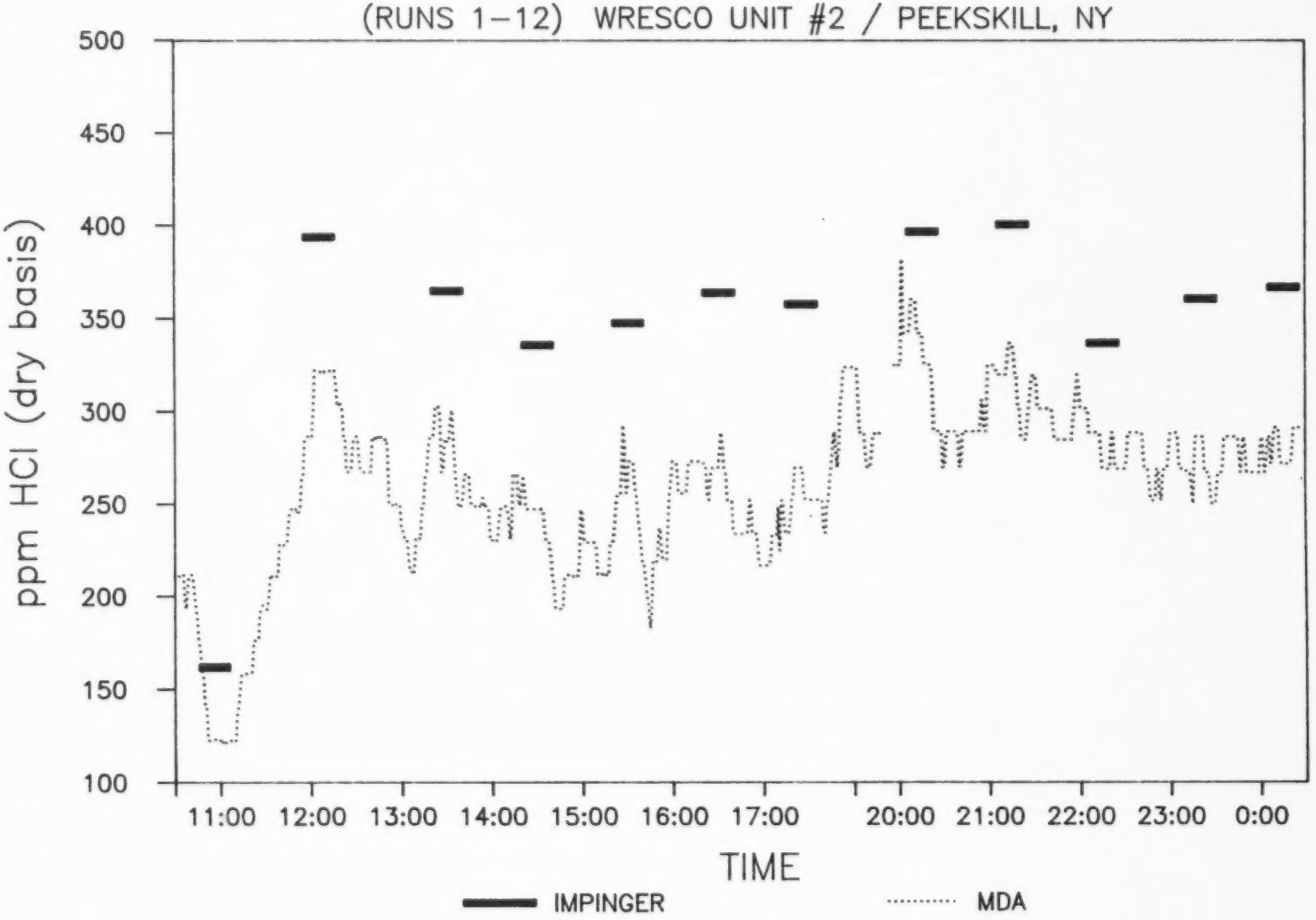


Figure A-14 **RELATIVE ACCURACY TEST – 3/20/87**

(RUNS 13–21) WRESCO UNIT #2 / PEEKSKILL, NY

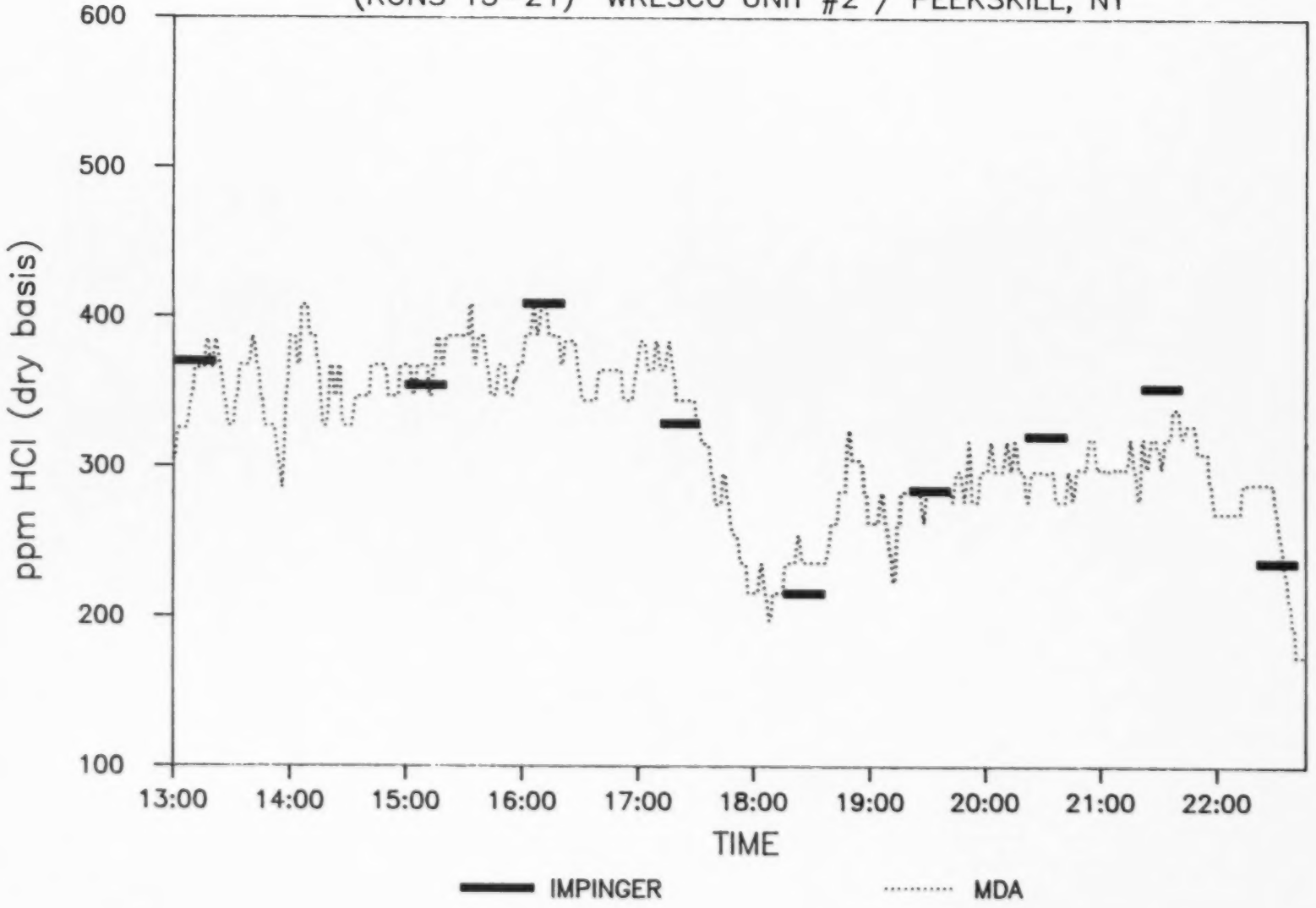


Figure A-15 **RELATIVE ACCURACY TEST - 4/27/87**

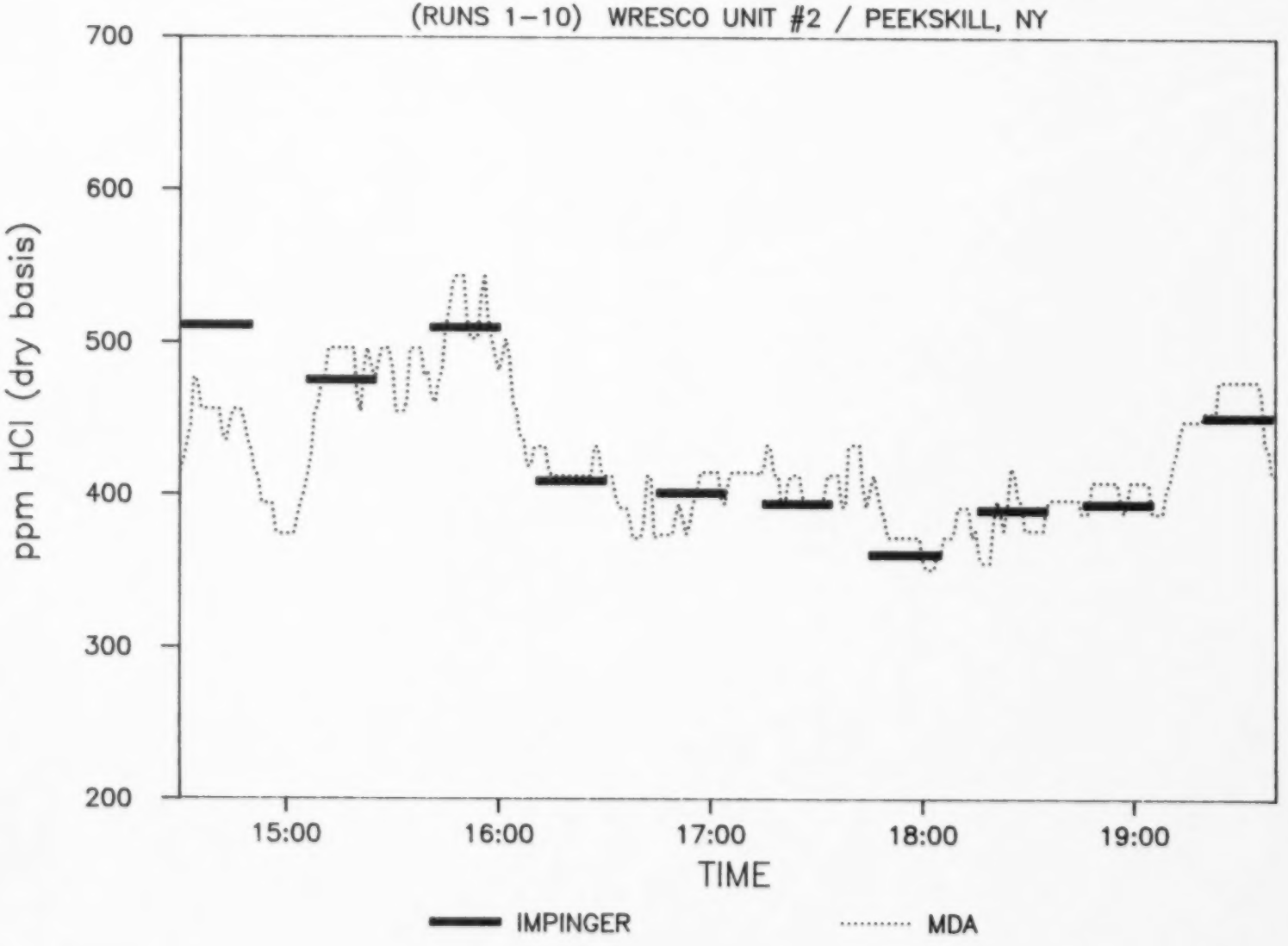
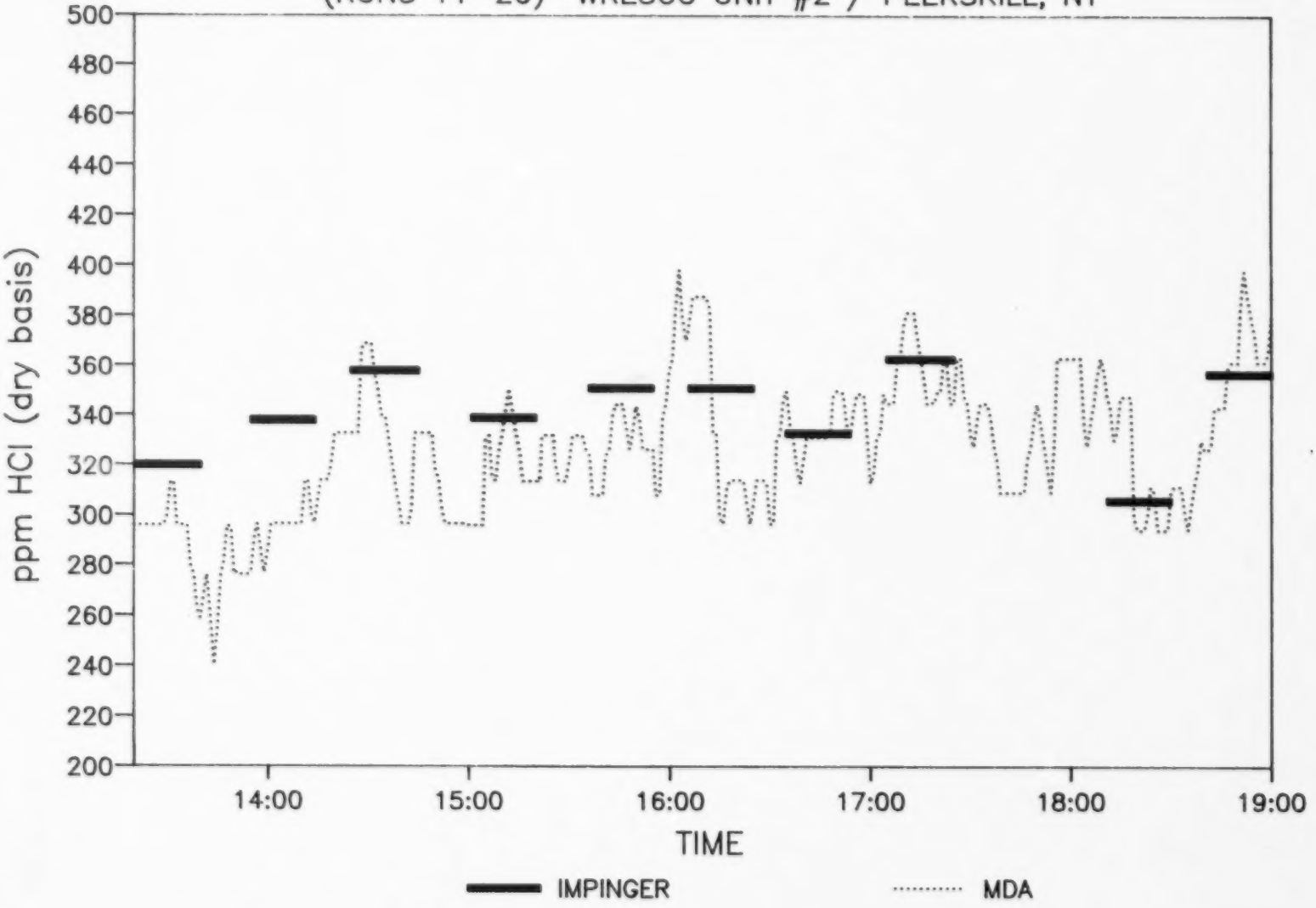


Figure A-16 **RELATIVE ACCURACY TEST - 4/29/87**

(RUNS 11-20) WRESCO UNIT #2 / PEEKSKILL, NY



- Individual Graphs During Relative Accuracy Periods

  - Compur

Figure A-17 **RELATIVE ACCURACY TEST – 3/19/87**

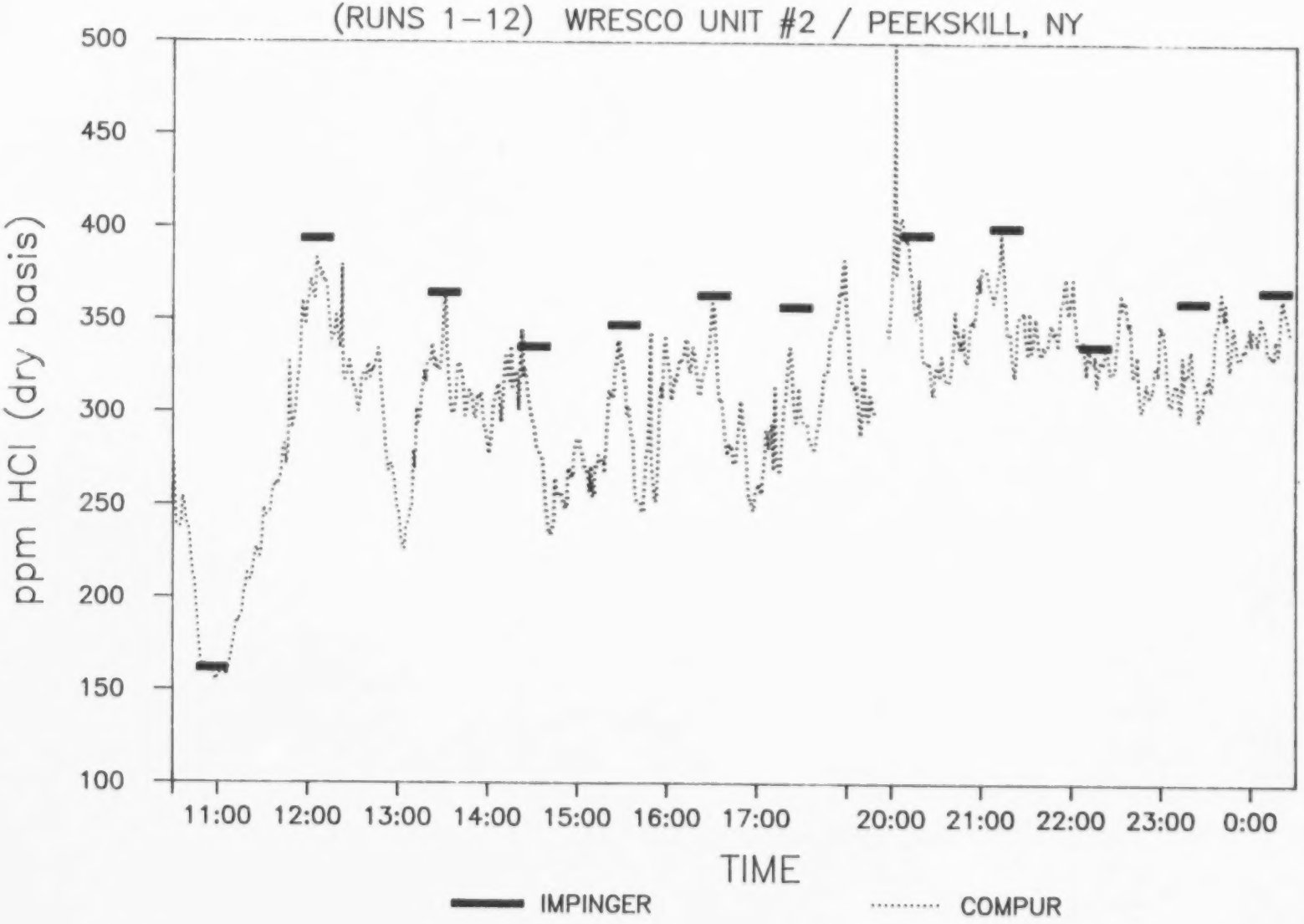


Figure A-18 **RELATIVE ACCURACY TEST – 3/20/87**

(RUNS 13–21) WRESCO UNIT #2 / PEEKSKILL, NY

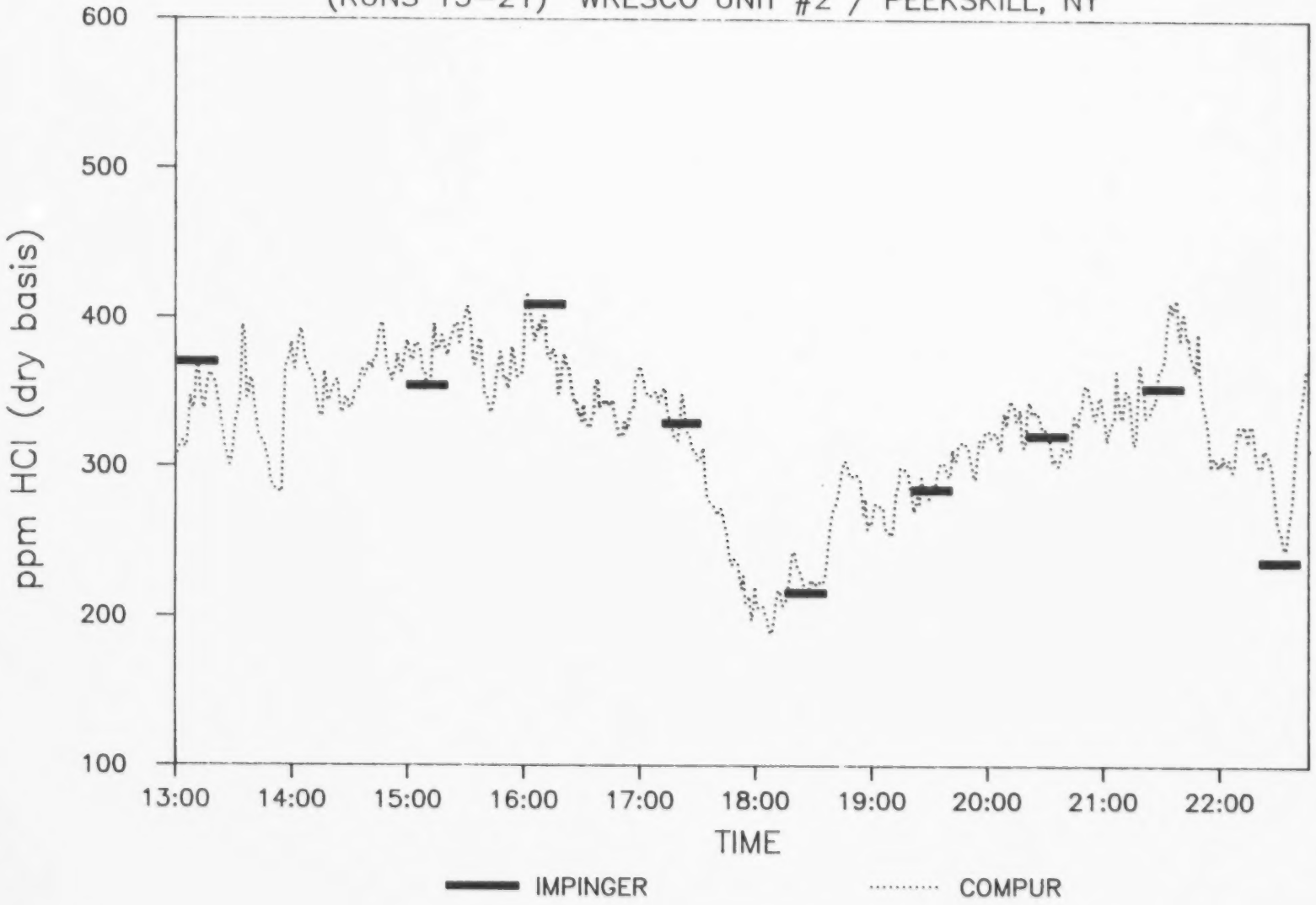


Figure A-19 **RELATIVE ACCURACY TEST – 4/27/87**

(RUNS 1–10) WRESCO UNIT #2 / PEEKSKILL, NY

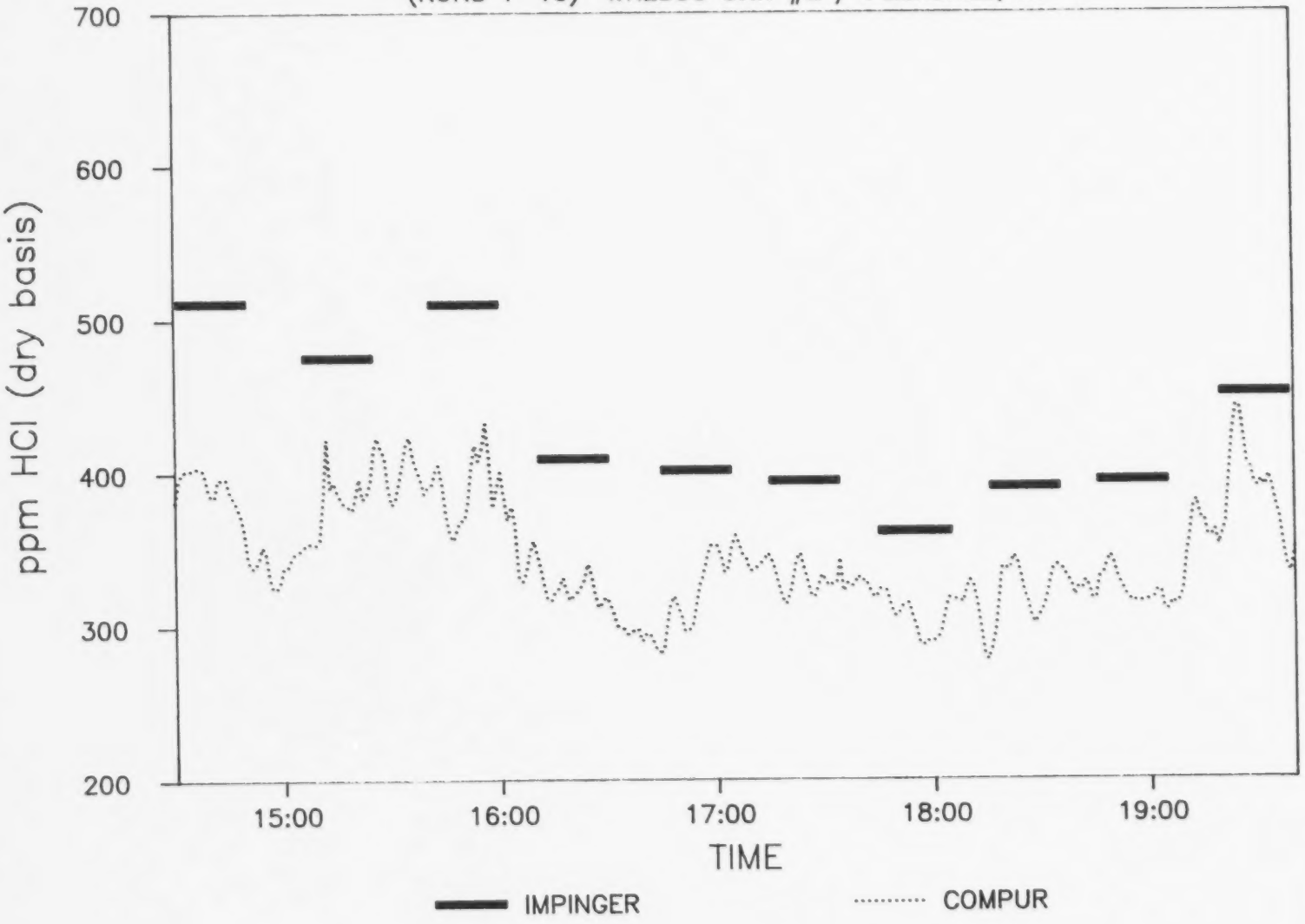
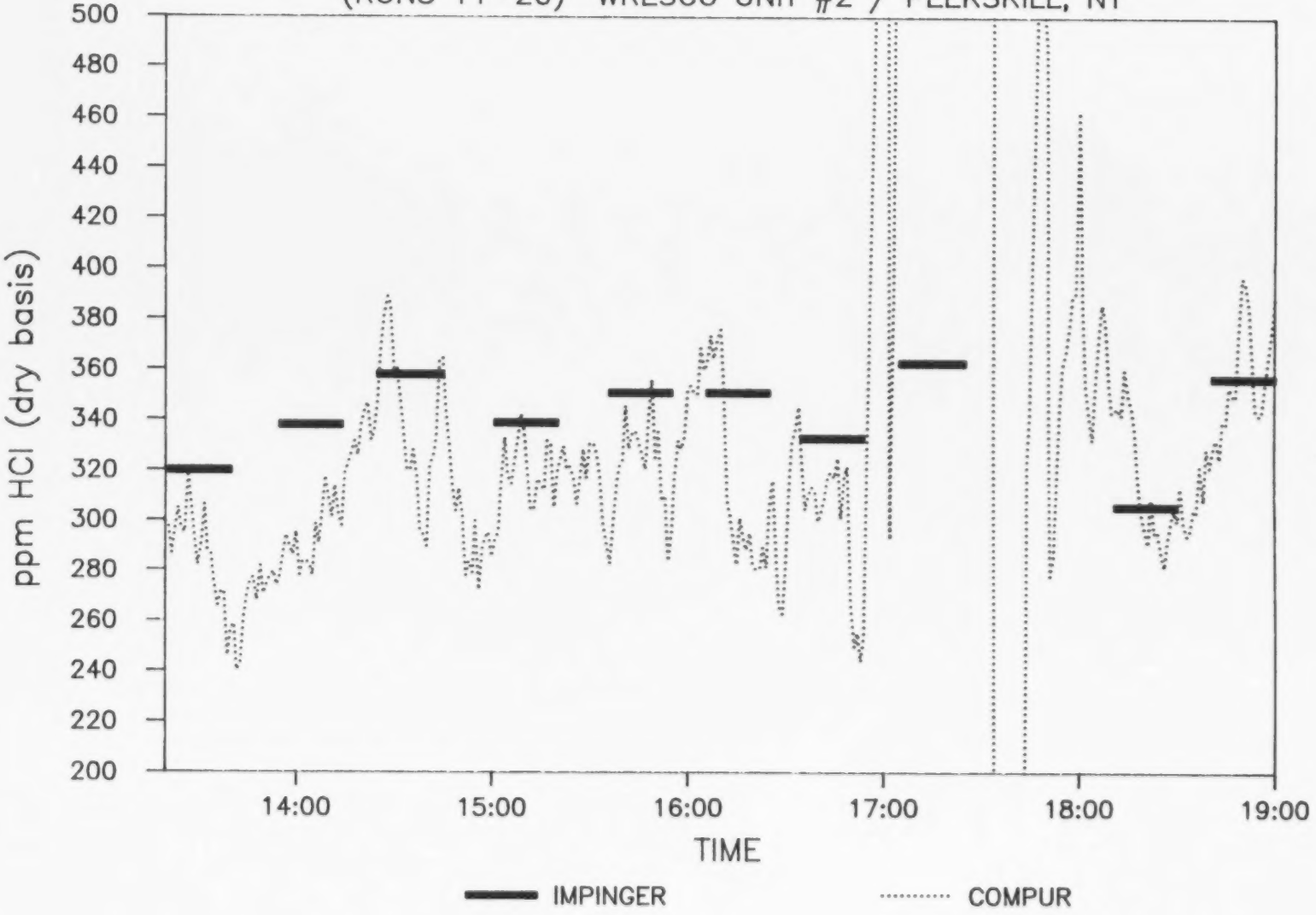


Figure A-20 **RELATIVE ACCURACY TEST – 4/29/87**

(RUNS 11–20) WRESCO UNIT #2 / PEEKSKILL, NY



APPENDIX B.

REFERENCE MEASUREMENTS FOR RELATIVE ACCURACY DETERMINATIONS

Table B-1

WESTCHESTER RESCO
RELATIVE ACCURCY TEST DATA

Compur Probe 40:1 - March 19-20, 1987

Run No.	Sample Times	Effluent % H_2O			Duct Impinger Sample (ppm HCl, dry)			Manifold Impinger Sample (ppm HCl, dry)			Corrected for Dilution
		Train A	Train B	Avg.	Train A	Train B	Avg.	Train A	Train B	Avg.	
1	1046-1106	10.9	10.9	10.9	164	160	162	3.6	2.4	3.0	141
2	1156-1216	12.1	12.1	12.1	388	400	394	7.7	6.9	7.3	343
3	1321-1341	11.8	11.5	11.7	358	371	365	6.4	5.9	6.2	291
4	1421-1441	10.3	11.6	11.0	336	337	336	5.8	5.5	5.7	268
5	1521-1541	14.2	13.7	14.0	341	355	348	5.8	5.7	5.8	273
6	1621-1641	12.7	12.9	12.8	366	363	364	6.5	6.3	6.4	301
7	1716-1736	12.0	13.7	12.9	358	357	358	6.3	6.0	6.2	291
8	2006-2026	12.6	13.1	12.9	408	387	397	7.3	7.0	7.2	338
9	2106-2126	11.7	11.3	11.5	394	408	401	6.8	6.6	6.7	315
10	2206-2226	12.9	12.5	12.7	341	333	337	6.4	6.0	6.2	291
11	2311-2331	12.1	11.8	12.0	355	366	361	6.2	6.1	6.2	291
12	0006-0026	13.9	13.0	13.5	362	372	367	6.8	6.4	6.6	310
TECO Probe 45:1 - March 20, 1987											
13	1301-1321	13.8	12.0	12.9	372	368	370	6.2	6.0	6.1	317
14	1501-1521	13.4	13.3	13.4	350	357	354	6.5	6.0	6.3	328
15	1601-1621	13.4	13.6	13.5	406	411	409	6.8	6.4	6.6	343
16	1711-1731	12.5	12.8	12.7	325	333	329	5.5	5.2	5.4	281
17	1816-1836	10.5	12.8	10.2	218	214	216	3.8	3.9	3.9	203
18	1921-1941	13.9	11.8	12.9	279	290	285	4.9	4.8	4.9	255
19	2021-2041	10.9	10.7	10.8	314	328	321	5.0	5.1	5.1	265
20	2121-2141	11.6	11.0	11.3	355	350	353	5.6	5.3	5.5	286
21	2221-2241	8.3	8.5	8.4	244	230	237	3.6	8.5	3.6	187

Table B-2

WESTCHESTER RESCO
RELATIVE ACCURCY TEST DATA

TECO Probe 45:1 - April 27, 1987

Run No.	Sample Times	Effluent % H_2O	Duct Impinger Sample (ppm HCl, dry)	Manifold Impinger Sample Sample (ppm HCl, dry)	Manifold Impinger Sample Corrected for Dilution
1	1431-1451	14.3	511	8.6	456
2	1506-1526	14.0	475	9.9	525
3	1541-1601	15.1	510	10.1	535
4	1611-1631	13.7	409	7.8	413
5	1646-1706	14.2	401	7.9	419
6	1716-1736	13.9	394	7.8	413
7	1746-1806	13.8	361	7.1	376
8	1816-1836	14.9	390	7.3	387
9	1846-1906	12.9	394	7.5	398
10	1921-1941	13.9	451	9.0	477
Compur Probe 40:1 - April 29, 1987					
11	1321-1341	14.2	320	6.5	306
12	1356-1416	14.4	338	6.4	301
13	1426-1446	14.4	358	7.3	343
14	1501-1521	14.2	339	7.0	329
15	1536-1556	12.7	351	6.7	315
16	1606-1626	14.4	351	5.8	273
17	1636-1656	14.0	333	6.1	287
18	1706-1726	13.0	363	6.6	310
19	1811-1831	13.7	306	5.4	254
20	1841-1901	12.6	357	6.3	296

APPENDIX C.

CALIBRATION DRIFT WORK SHEETS

Figure C-1 **CALIBRATION DRIFT**

SOURCE AND LOCATION WRESCO - Unit #2 ESP Outlet

MONITOR Bodenseewerk 677 HCl Monitoring System (0-1000 ppm)

DAY	DATE/TIME		CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE	PERCENT SPAN	
1	3/13/87	Midnight 0000	0 (zero air)	0	0	0%	
2	3/14/87	0000	0	0	0	0%	
3	3/15/87	0000	0	0	0	0%	
4	3/16/87	0000	0	0	0	0%	
5	3/17/87	0000	0	0	0	0%	
6	3/18/87	0000	0	-2	-2	0.2%	LOW LEVEL
7	3/19/87	0000	0	-3	-3	0.3%	
8	3/20/87	0600	0	-2	-2	0.2%	
	3/20/87	0130	0 (zero air)	-2	-2	0.2%	
	4/23/87	1430	0 (zero air)	1	1	0.1%	
1	3/13/87	Midnight 0000	505 (cell)	510	5	0.5%	
2	3/14/87	0000	505	505	0	0%	
3	3/15/87	0000	505	508	3	0.3%	
4	3/16/87	0000	505	508	3	0.3%	
5	3/17/87	0000	505	510	5	0.5%	
6	3/18/87	0000	505	510	5	0.5%	HIGH LEVEL
7	3/19/87	0000	505	509	4	0.4%	
8	3/20/87	0600	505	508	3	0.3%	
	3/20/87	0130	479 (cal gas)	472	-7	0.7%	
	4/23/87	1430	503 (cal gas)	500	-3	0.3%	

Figure C-2 **CALIBRATION DRIFT**

SOURCE AND LOCATION WRESCO - Unit #2 ESP Outlet

MONITOR MDA 7100 HCl Analyzer / TECO 200 Dilution System (45:1)
(100 ppm HCl analyzer operating range) / Compur Dilution System (40:1)

DAY	DATE/TIME		CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE	PERCENT SPAN
1	3/2/87	1555	0	0	0	0%
2	3/3/87	1235	0	1	1	0%
3	3/4/87	1250	0	1	1	0%
4	3/5/87	1110	0	1	1	
1	3/18/87	1630	0	1	1	0%
2	3/19/87	0900	0	1	1	0%
3	3/20/87	0130	0	0	0	0%
1	3/27/87	0900	0	3	3	0.1%
2	3/31/87	1200	0	3	3	0.1%
3	4/1/87	0930	0	3	3	0.1%
4	4/2/87	1400	0	3	3	0.1%
1	4/15/87	1200	0	3	3	0.1%
2	4/16/87	0900	0	3	3	0.1%
3	4/21/87	1700	0	3	3	0.1%
4	4/22/87	1120	0	2	2	0.1%
1	3/2/87	1555	479	825	346	7.7%
2	3/3/87	1235	479	815	336	7.5%
3	3/4/87	1250	479	825	346	7.7%
4	3/5/87	1110	479	670	191	4.8%
1	3/18/87	1630	479	486	7	0.2%
2	3/19/87	0900	479	627	148	3.7%
3	3/20/87	0130	479	562	83	2.1%
1	3/27/87	0900	439	644	205	5.1%
2	3/31/87	1200	439	834	395	9.9%
3	4/1/87	0930	439	661	222	5.6%
4	4/2/87	1400	479	505	26	0.7%
1	4/15/87	1200	503	490	-13	0.3%
2	4/16/87	0900	503	458	-45	1.1%
3	4/21/87	1700	503	614	111	2.8%
4	4/22/87	1120	503	426	-77	1.9%

LOW LEVEL

HIGH LEVEL

Figure C-3 **CALIBRATION DRIFT**

SOURCE AND LOCATION WRESCO - Unit #2 ESP Outlet

MONITOR Compur 2GSM HCl Analyzer / Compur Dilution System (40:1)

DAY	DATE/TIME		CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE	PERCENT SPAN	
1	3/18/87	1630	0	23	23	0.7%	
2	3/19/87	0900	0	30	30	0.9%	
3	3/20/87	0130	0	31	31	0.9%	
1	3/27/87	0900	0	32	32	1.0%	
2	3/31/87	1200	0	23	23	0.7%	
3	4/1/87	0930	0	16	16	0.5%	
4	4/2/87	1400	0	19	19	0.6%	
1	4/15/87		0	65	65	1.9%	LOW LEVEL
2	4/16/87		0	35	35	1.0%	
3	4/21/87		0	90	90	2.7%	
1	3/18/87	1630	479	445	-34	1.0%	
2	3/19/87	0900	479	502	23	0.7%	
3	3/20/87	0130	479	492	13	0.4%	
1	3/27/87	0900	439	400	-39	1.2%	
2	3/31/87	1200	439	387	-52	1.6%	
3	4/1/87	0930	439	327	-112	3.3%	
4	4/2/87	1400	479	400	-79	2.4%	HIGH LEVEL
1	4/15/87	1200	503	505	2	0.1%	
2	4/16/87	0900	503	660	157	4.7%	
3	4/21/87	1700	503	500	-3	0.1%	

Figure C-4 **CALIBRATION DRIFT**

SOURCE AND LOCATION WRESCO Unit #2 ESP Outlet

MONITOR TECO 15 HCl Analyzer / TECO 200 Dilution System (45:1)
(100 ppm HCl analyzer operating range) Compur Dilution System (40:1)

DAY	DATE/TIME		CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE	PERCENT SPAN	
1	3/2/87	1555	0	0	0	0%	TECO ↓ Compur
2	3/3/87	1235	0	58	58	1.3%	
3	3/4/87	1250	0	45	45	1.0%	
4	3/5/87	1110	0	40	40	1.0%	
1	3/18/87	1630	0	2	2	0.1%	
2	3/19/87	0900	0	5	5	0.1%	
3	3/20/87	0130	0	27	27	0.7%	
							LOW LEVEL
1	3/27/87	0900	0	10	10	0.3%	
2	3/31/87	1200	0	43	43	1.1%	
3	4/1/87	0930	0	15	15	0.4%	
4	4/2/87	1400	0	35	35	0.9%	
1	4/15/87	1200	0	0	0	0%	
2	4/16/87	0900	0	12	12	0.3%	
3	4/21/87	1700	0	20	20	0.5%	
4	4/22/87	1120	0	0	0	0%	
1	3/2/87	1555	479	456	-23	0.5%	
2	3/3/87	1235	479	541	62	1.4%	
3	3/4/87	1250	479	528	49	1.1%	
4	3/5/87	1110	479	515	36	0.9%	
1	3/18/87	1630	479	507	28	0.7	
2	3/19/87	0900	479	493	14	0.4	
3	3/20/87	0130	479	532	53	1.3	
							HIGH LEVEL
1	3/27/87	0900	439	410	-29	0.7%	
2	3/31/87	1200	439	439	0	0%	
3	4/1/87	0930	439	425	-14	0.4%	
4	4/2/87	1400	479	455	16	0.4%	
1	4/15/87	1200	503	525	22	0.6%	
2	4/16/87	0900	503	513	10	0.3%	
3	4/21/87	1700	503	528	25	0.6%	
4	4/22/87	1120	503	512	9	0.2%	

Figure C-5 **CALIBRATION DRIFT**

SOURCE AND LOCATION WRESCO Unit #2 ESP Outlet

MONITOR LSI/CEA TGM-555 HCl Analyzer / TECO 200 Dilution System (45:1)
(50 ppm HCl analyzer operating range) Compur Dilution System (40:1)

DAY	DATE/TIME		CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE	PERCENT SPAN	Sampling System
1	3/2/87	1555	0	0	0	0%	TECO
2	3/3/87	1235	0	20	20	0.9%	
3	3/4/87	1250	0	17	17	0.8%	
4	3/5/87	1110	0	20	20	1.0%	
							Compur
1	3/18/87	1630	0	6	6	0.3%	
2	3/19/87	0900	0	12	12	0.6%	
3	3/20/87	0130	0	15	15	0.8%	
							LOW LEVEL
1	3/27/87	0900	0	4	4	0.2%	
2	3/31/87	1200	0	0	0	0%	
3	4/1/87	0930	0	27	27	1.4%	
4	4/2/87	1400	0	2	2	0.1%	
1	4/16/87	0900	0	10	10	0.5%	
2	4/21/87	1700	0	-43	-43	2.2%	
3	4/22/87	1120	0	14	14	0.7%	
1	3/2/87	1555	479	473	-6	0.3%	TECO
2	3/3/87	1235	479	450	-29	1.3%	
3	3/4/87	1250	479	478	-1	0%	
4	3/5/87	1110	479	453	-26	1.3%	
							Compur
1	3/18/87	1630	479	479	0	0%	
2	3/19/87	0900	479	454	-25	1.3%	
3	3/20/87	0130	479	494	15	0.8%	
							HIGH LEVEL
1	3/27/87	0900	439	410	-29	1.5%	
2	3/31/87	1200	439	400	-39	2.0%	
3	4/1/87	0930	439	420	-19	1.0%	
4	4/2/87	1400	479	429	-50	2.5%	
1	4/16/87	0900	503	518	15	0.8%	
2	4/21/87	1700	503	420	-83	4.2%	
3	4/22/87	1120	503	522	19	1.0%	

APPENDIX D.

CALIBRATION ERROR WORKSHEETS

Figure D-1 CALIBRATION ERROR DETERMINATION

Source and Location LIGNITE RESEARCH COUNCIL - Unit #2 ESP Outlet 4/22/87

Monitor LSI/CEA TGM 555 HCl analyzer / Comput Sampling System (40:1)

HCl Calibration Gas

High Range _____

Mid Range 1556 ppm

Low Range 503 ppm

Zero Air

Run #	Calibration Gas Concentration, ppm/ %				Measurement System Reading, ppm/ %				Differences, ppm/ %			
	Zero	Low	Mid	High	Zero	Low	Mid	High	Zero	Low	Mid	High
1	0				14				14			
2		503				522				19		
3	0				25				25			
4		503				510				7		
5			1556				970				-586	
6		503				508				5		
7	0				22				22			
8		503				500				-3		
9			1556				972				-584	
10	0				18				18			
11			1556				972				-584	
12		503				513				10		
13			1556				978				-578	
14		503				520				17		
15			1556				978				-578	
16												
17												
18												
19												
20												
Mean Difference =									19.8	9.2	-582	
Confidence Interval =									/	8.5	4.6	
Calibration Error = $\frac{\lvert\text{Mean Difference}\rvert + \text{C.I.}}{\text{Avg. Calibration Gas Concentration}} \times 100$ =									/ %	3.5 %	37.7 %	%

Figure D-2 CALIBRATION ERROR DETERMINATION

Source and Location WRESCO - Unit #2 ESP Outlet 4/22/87

Monitor TECO 15 HCl analyzer / Comput Sampling System

HCl Calibration Gas

High Range _____

Mid Range 1556 ppm

Low Range 503 ppm

Zero Air

Run #	Calibration Gas Concentration, ppm/ %				Measurement System Reading, ppm/ %				Differences, ppm/ %			
	Zero	Low	Mid	High	Zero	Low	Mid	High	Zero	Low	Mid	High
1	0				0				0			
2		503				512				9		
3	0				0				0			
4		503				517				14		
5			1556				1510				-46	
6		503				533				30		
7	0				8				8			
8		503				509				6		
9			1556				1553				-3	
10	0				20				20			
11			1556				1553				-3	
12		503				545				42		
13			1556				1550				-6	
14		503				541				38		
15			1556				1558				2	
16	0				20				20			
17												
18												
19												
20												
Mean Difference =									9.6	23.2	-11.2	
Confidence Interval =									/	16.3	24.4	
Calibration Error = |Mean Difference| + C.I. / Avg. Calibration Gas Concentration x 100 =									/ %	7.9 %	2.3 %	%

Figure D-3 CALIBRATION ERROR DETERMINATION

Source and Location WRESCO - Unit #2 ESP Outlet 4/22/87

Monitor MDA Model 7100 HCl analyzer / Compu Sampling System

HCl Calibration Gas

High Range _____

Mid Range 1556 ppm

Low Range 503 ppm

Zero Air

Run #	Calibration Gas Concentration, ppm/ %				Measurement System Reading, ppm/ %				Differences, ppm/ %			
	Zero	Low	Mid	High	Zero	Low	Mid	High	Zero	Low	Mid	High
1	0				2		repeated dynamic cal					
2		503	Re-start			426						
3	0				2				2			
4		503				505				2		
5			1556				1320				-236	
6		503				528				25		
7	0				3				3			
8		503				536				33		
9			1556				1337				-219	
10	0				3				3			
11			1556				1306				-250	
12		503				536				33		
13			1556				1385				-171	
14		503				583				80		
15			1556				1368				-188	
16	0				3				3			
17												
18												
19												
20												
Mean Difference =									2.8	34.6	-213	
Confidence Interval =									/	35.2	41	
									%	13.9 %	16.3 %	%

$$\text{Calibration Error} = \frac{|\text{Mean Difference}| + \text{C.I.}}{\text{Avg. Calibration Gas Concentration}} \times 100 =$$

Figure D-4 CALIBRATION ERROR DETERMINATION

Source and Location WRESCO - Unit #2 ESP Outlet 4/22/87

Monitor Compur

HCl Calibration Gas

High Range _____

Mid Range 1556 ppm

Low Range 503 ppm

Zero Air

ENTROPY

Run #	Calibration Gas Concentration, ppm/ %				Measurement System Reading, ppm/ %				Differences, ppm/ %			
	Zero	Low	Mid	High	Zero	Low	Mid	High	Zero	Low	Mid	High
1	0				SYSTEM FAULT							
2		503										
3	0				22				22			
4		503				500				-3		
5			1556				1640				84	
6		503				517				14		
7	0				26				26			
8		503				505				2		
9			1556				1671				115	
10	0				32				32			
11			1556				1684				128	
12		503				539				36		
13			1556				1724				168	
14		503				529				26		
15			1556				1639				83	
16	0				43				43			
17												
18												
19												
20												
Mean Difference =									31	15.0	115.6	
Confidence Interval =									/	20.2	43.7	
Calibration Error = $\frac{\lvert\text{Mean Difference}\rvert + \text{C.I.}}{\text{Avg. Calibration Gas Concentration}} \times 100$ =									/ %	7.0 %	10.2 %	%

Figure D-5 CALIBRATION ERROR DETERMINATION

Source and Location _____

Monitor LSI / Comgw probe

Calibration Gas

High Range _____

Mid Range _____

Low Range _____

Zero _____

ENTROPY

Run #	Calibration Gas Concentration, ppm/ %				Measurement System Reading, ppm/ %				Differences, ppm/ %			
	Zero	Low	Mid	High	Zero	Low	Mid	High	Zero	Low	Mid	High
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												
Mean Difference =												
Confidence Interval =												
Calibration Error = $\frac{\lvert\text{Mean Difference}\rvert + \text{C.I.}}{\text{Avg. Calibration Gas Concentration}} \times 100 =$									%	%	%	%

Not tested due to long response time and shortage of cal gas

Figure D-6 CALIBRATION ERROR DETERMINATION

Source and Location WRESCO Unit #2 ESP Outlet 4/22/87

Monitor TECO Model 15 HCl Analyzer/ TECO 200 Dilution probe (45:1)

HCl Calibration Gas

High Range _____

Mid Range 1556 ppm

Low Range 503 ppm

Zero Air

Run #	Calibration Gas Concentration, ppm/ %				Measurement System Reading, ppm/ %				Differences, ppm/ %			
	Zero	Low	Mid	High	Zero	Low	Mid	High	Zero	Low	Mid	High
1	0				0				0			
2		503				500				-3		
3			1556				1428				-128	
4	0				20				20			
5			1556				1437				-119	
6		503				509				6		
7	0				23				23			
8		603				505				2		
9			1556				1450				-106	
10		503				520				17		
11			1556				1450				-106	
12		503				516				13		
13			1556				1450				-106	
14												
15												
16												
17												
18												
19												
20												
									14.3	7.0	-113.0	
									/	10.0	12.5	
									/ %	3.4 %	8.1 %	%

Mean Difference =

Confidence Interval =

$$\text{Calibration Error} = \frac{|\text{Mean Difference}| + \text{C.I.}}{\text{Avg. Calibration Gas Concentration}} \times 100 =$$

Figure D-7 CALIBRATION ERROR DETERMINATION

Source and Location WRESCO Unit #2 ESP Outlet 4/22/87

Monitor MDA 7100 HCl Analyzer / TECO 200 Dilution probe (45:1)

HCl Calibration Gas

High Range _____

Mid Range 1556 ppm

Low Range 503 ppm

Zero Air

Run #	Calibration Gas Concentration, ppm/ %				Measurement System Reading, ppm/ %				Differences, ppm/ %			
	Zero	Low	Mid	High	Zero	Low	Mid	High	Zero	Low	Mid	High
1	0				3				3			
2		503				500				-3		
3			1556				1256				-300	
4	0				3				3			
5			1556				1239				-317	
6		503				533				30		
7	0				3				3			
8		503				480				-23		
9			1556				1239				-317	
10		503				533				30		
11			1556				1345				-211	
12		503				533				30		
13			1556				1327				-229	
14												
15												
16												
17												
18												
19												
20												
									3	12.8	-275	
									/	30.5	63	
									/ %	8.6 %	21.7 %	%

Mean Difference =

Confidence Interval =

$$\text{Calibration Error} = \frac{|\text{Mean Difference}| + \text{C.I.}}{\text{Avg. Calibration Gas Concentration}} \times 100 =$$

APPENDIX E.

DOCUMENTATION CONCERNING MOISTURE BASIS READINGS OF BODENSEEWERK HC1 CEM

BODENSEEWERK Bodenseewerk Gerätetechnik GmbH Überlingen

Fax Nr./No. _____ Seitenzahl/No. of Pages: 1 Datum/Date: 22-9-1987

AN/TO:	VON/FROM: BODENSEEWERK GERÄTETECHNIK GMBH	
K V B attn. Mr. Jim Nelsen 18006 Skypark Blvd., Irvine, California 92714	Bereich/Abteilg. / Division, Department: Geosystem Dr. W. Berkhahn	
Telefax-Rufnummer/No.: 001-714-250-9015	Telefax-Rufnummer/No.: 07532-801-104	
Telefon Nr.:/Phone No.: 001-714-250-6200	Telefon Nr.:/Phone No.: 07532/801-100	Kostenstelle: 2500

Mitteilung/Message:

Subject: Dry measurement basis of HCl with a Bodenseewerk System -
Your fax, dated 11-9-1987

The HCl-system, tested by EPA, was calibrated with 15 Vol./% H_2O. The concentration reading corresponds to a dry measurement. The reading is exact for 15 Vol./%, the error of reading is less than 4 Vol./% of the full scale for variation of water vapor between 0 Vol./% of water vapor up to 20 Vol./%. The documents concerning the calibration were given to Ron Jernigan and with separate cover you will get a report, concerning the problems of dry and wet reading in German and a translation of this report which you can correct, if necessary.

Kind regards,

BODENSEEWERK GERÄTETECHNIK GMBH
Geosystem

(W. Berkhahn)

RECEIVED
SEP 29 1987
NSF

cc: cc. Berkhahn

V.-Nr. 3-690/8703

Influence of water vapour variations in stack gas on HCl measurement, if the read out of HCl is related to dry gas

1. Introduction

According to the new technical instructions for Maintaining Air Purity (TA-Luft) the reading of an HCl-monitoring system has to be related to dry gas. Due to the fact, that the photometric HCl-measurement can only be done at temperatures above dew point, the removing of water vapour by gas cooling devices is not possible. If there would not be any influence of water vapour on the HCl-measurement, the read out related to dry gas would only be possible if the water vapour content is known and a calculation is done. If the HCl-concentration is measured by an IR-photometer, molecular interactions between HCl and H_2O cause an increase of sensitivity to HCl with increasing water vapour content. This effect can be used for compensating partially the dilution effect caused by water vapour if the HCl concentration is measured related to dry gas. The calibration procedure should be done according to the calibration procedure done for wet measurement at the average water vapour content of the plant. The reading error caused by water vapour variations in the flue gas should then be less than the dilution effect and within the allowed reading error of the instrument.

2. Test procedure

The tests have been made with a standard HCl-measuring system with serial number S/N 569. The system has been equipped with a heated long path cell adjusted to 10 m optical path length. The calibration was made with the standard calibration unit. The photometer was adjusted to have no signal offset between 0 to 30 Vol.-% water vapour. HCl/N_2 mixtures were set to about 50, 100, 150 and 200 mg/Nm³.

At each concentration water vapour was added to have moisture contents between 0 and 20 Vol.-% without changing the HCl-/N_2-flow.

3. Test results

With the test procedure described in 2.) the following results have been obtained (Table 1):

HCl-Conc. $(mg/Nm^3)_{dry}$ Set values	H_2O-Conc. (Vol.-%) 0	10	15	20
0	0	0	0	0
49,4	2,75	2,55	2,45	2,30
105	5,00	4,85	4,70	4,50
150	6,30	6,20	6,05	5,85
203	7,70	7,80	7,70	7,50

Table 1: Measuring results of the HCl-photometer at variations of HCl- and H_2O-concentrations. (Measuring values are in absorbance units x 10^{-3}).

According to the procedure mentioned in 1.) the calibration was made at 15 Vol.-% moisture content, but the read out of the instrument was given in mg/Nm³ HCl related to dry gas. The measuring range was set to 0 - 200 mg/Nm³ HCl. The calibration values have been calculated for linearizing using a least square fit (Fig. 1). Using the lienarized curve the HCl-concentrations used for calibration have been calculated. These calculated concentrations have been furtheron used as our reference values.

Set values /	Calculated values
0	0
49,4	48,8
105	107,0
150	147,7
203	204,0

Tabel 2: Calculation of the HCl-calibration concentrations (read out in mg/Nm³, dry gas).

The absorbance values obtained at moisture contents of 0, 10 and 20 Vol.-% have now been used for calculating the HCl-read out on basis of the calibration curve at 15 Vol.-% H_2O (Table 3).

HCl-Conc. $(mg/Nm^3)_{dry}$ calculated at 15 Vol.-% H_2O	H_2O-Conc. (Vol.-%) 0	10	15	20
0	0	0	0	0
48,8	55,9	51,1	48,8	45,4
107,0	115,7	109,9	107,0	101,4
147,7	155,7	152,5	147,7	141,4
204,0	204,0	207,7	204,0	196,7

Table 3: Photometer read out in mg/Nm³ HCl dry gas at different water vapour concentrations

In Fig. 2. these measuring values are shown graphically.

For estimating the accuracy of an instrument, the reading error related to the full scale of the instrument is the most important. Therefore the deviation of the photometer read out related to 200 mg/Nm³ dry gas is reported in table 4.

HCl-Conc. $(mg/m^3)_{dry}$ calculated at 15 Vol.-% H_2O	H_2O-Conc. (Vol.-%) 0	10	15	20
0	0	0	0	0
48,8	3,6	1,2	0	- 1,7
107,0	4,4	1,5	0	- 2,8
147,7	4,0	2,4	0	- 3,2
204,0	0	1,9	0	- 3,7

Table 4: Deviation of instrument read out in percent fs at different moisture concentrations.

In Fig. 3 these deviations are shown graphically.

4. Conclusion

The test measurements show that if the read out is related to dry gas the deviation caused by water vapour variations in the flue gas is suppressed. If the HCl measuring system is calibrated at the average moisture content in the flue gas, the reading errors caused by water vapour variations are within the limits, set by the Federal Immissions Control law for emission monitoring systems.

V-Nr 3-619

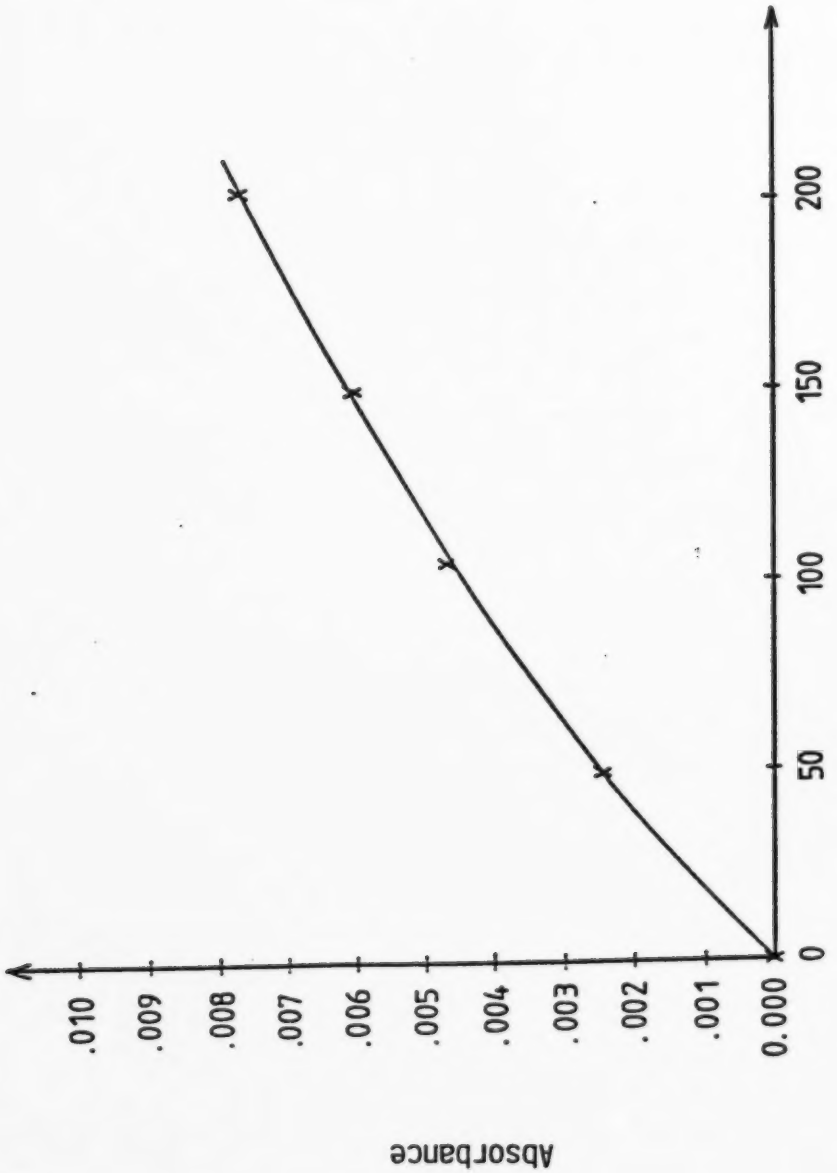
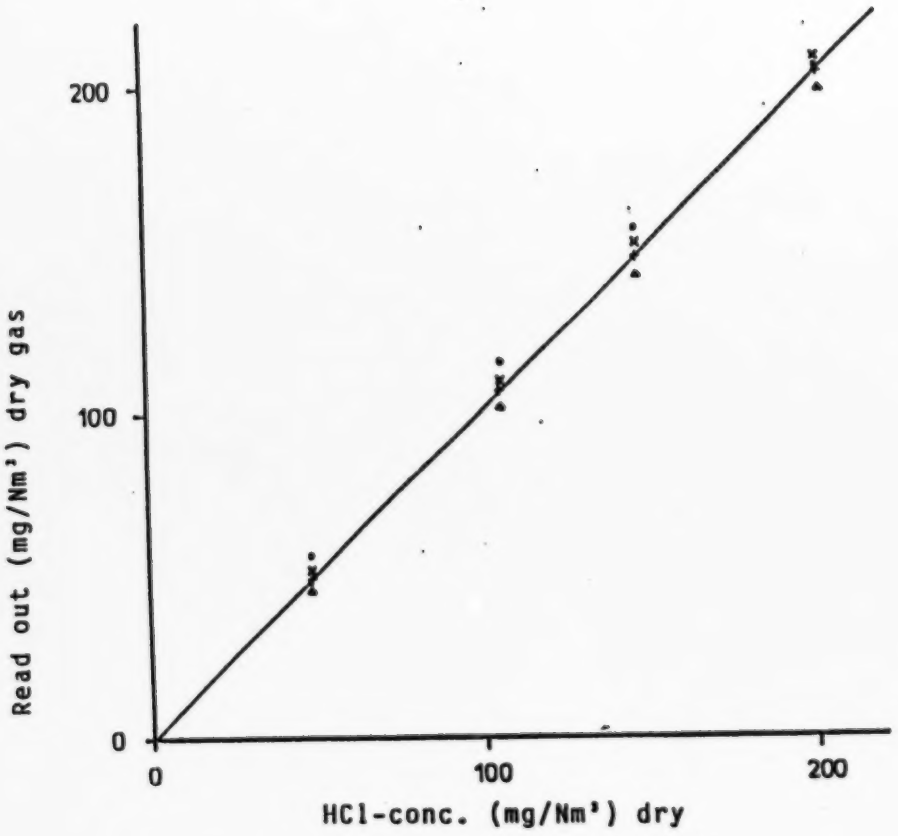


Fig. 1: HCl-concentration (mg/Nm³) dry



H_2O- content

- • 0 Vol-%
- × 10 Vol-%
- + 15 Vol-%
- ▲ 20 Vol-%

Fig. 2: Read out in mg/Nm³ HCl, dry,
at different water vapour concentrations

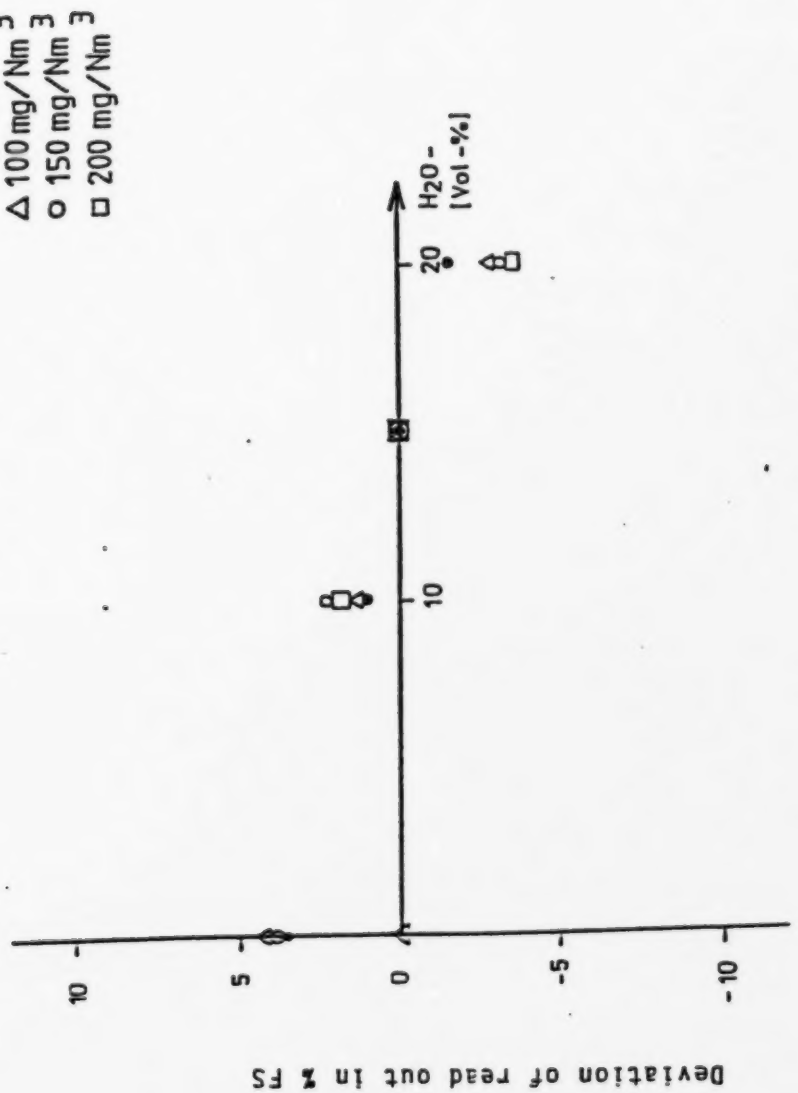


Fig. 3: Deviation of read out in % FS
at different water vapour concentrations